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INVESTIGATIONS ON THE CONNECTION OF POLARIZATION AND FOREIGN QUENCHING IN FLUORESCENT SOLUTIONS

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At variance with earlier results, the true degree of polarization of fluorescence (the value corrected for secondary luminescence) has been found to depend linearly on the relative quantum yield for fluorescein dissolved in water and quenched with KI. The quenching of fluorescein and trypaflavine with KI was found to be of pure dynamic character. A formula for the connection of the degree of polarization of fluorescence and the concentration of quencher is given and experimentally proved.

Introduction

1. A study of the degree of polarization of fluorescence of solutions quenched by foreign substances may give valuable informations about the character of the quenching process. In case of dynamic quenching the increase of concentration of quencher causes a diminution of the mean life time of fluorescence, consequently a decrease of the rotational depolarization and thus an increase of the degree of polarization, while in case of static quenching the degree of polarization does not depend on the concentration of quencher.

According to F. PERRIN [1] the degree of polarization of *unquenched fluorescence*, p_0, may be given by the equation

$$\frac{1}{p_0}-\frac{1}{3}=\left(\frac{1}{p_\infty}-\frac{1}{3}\right)\left(1+\frac{kT}{V\eta_v}\tau_0\right), \tag{1}$$

where p_0, k, T, τ_0, V and η_v denote the limiting polarization ($p_0 \to p_\infty$ if $\eta_v \to \infty$ or $\tau_0 \to 0$), the Boltzmann-constant, the absolute temperature of the solution, the mean life time of the excited state, the molar volume of the solute molecule (including the solvent layer) and the viscosity of the solution, respectively. For the degree of polarization of quenched fluorescence of solutions, p, the following equations hold:

$$\frac{1}{p}-\frac{1}{3}=\left(\frac{1}{p_0}-\frac{1}{3}\right)\left(1+\frac{kT}{V\eta_v}\tau\right), \tag{2}$$

or, provided T, V and η_v remain unchanged during the quenching process,

$$\frac{1}{p}-\frac{1}{p_\infty}=\left(\frac{1}{p_0}-\frac{1}{p_\infty}\right)\frac{\tau}{\tau_0}, \tag{3}$$

where τ denotes the mean life time of the excited state for quenched fluorescence. When $\tau/\tau_0 = \eta/\eta_0$ (η/η_0 is the relative yield of fluorescence),

$$\frac{1}{p} - \frac{1}{p_\infty} = \left(\frac{1}{p_0} - \frac{1}{p_\infty}\right)\frac{\eta}{\eta_0}, \tag{4}$$

thus $1/p$ is a linear function of η/η_0.

2. Experiments showed that the linearity of the function $1/p = f(\eta/\eta_0)$ is fulfilled for fluorescein [2], fluorescein and rhodamin B [3] in glycerol-water mixture, fluorescein [1], rhodamin B [4] in water quenched by KI, but it is not valid for rhodamin B and riboflavine [5] in water quenched by hydrochinone, 3-amino-pyrene-8, 10-trisulfonate [6] in water quenched by different organic compounds and for fluorescein [7—8] in water quenched by KI. The divergence from linearity may be explained by assuming a mixed type of quenching, in which case $\tau/\tau_0 \neq \eta/\eta_0$, thus eq. (4) should not hold. In [2], [3], [8] and [9] different relations to be substituted into eq. (3) are given instead of $\tau/\tau_0 = \eta/\eta_0$, in [7] a new equation was derived to explain the non-linearity observed.

A comparison of experimental data obtained by different authors for fluorescein in water quenched by KI exhibits comparatively large deviations which should justify the assumption of contradictory quenching mechanisms (Fig. 1). In [7] the law of decay was supposed to be non-exponential, in [9] an initial static quenching was considered, in [1] an exponential law of decay and the role of BROWNian rotation was taken into account.

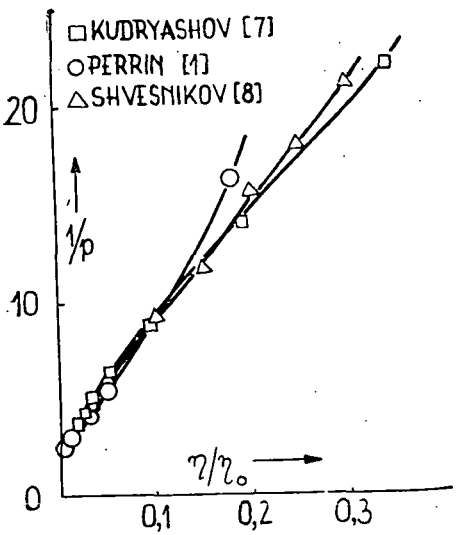

Fig. 1

The aim of the present work was to repeat with greater accuracy the investigations about the system mentioned and to carry out further experiments allowing to draw some conclusions concerning the relation between the degree of polarization of fluorescence and concentration of quencher in the systems investigated.

Experimental

1. The degree of polarization of fluorescence has been measured by a photoelectric apparatus and a method described in [10] at a temperature of 30,0± 0,1 °C. The excitation of the fluorescence of fluorescein and trypaflavine was carried out on a wavelength of 436 mμ and 460 mμ, respectively. The temperature of the samples was maintained by a Höppler ultrathermostat and measured by means of a thermistor (2TH65) attached to the wall of the sample holder. The viscosities of the samples were measured by a Höppler viscosimeter at a temperature of 30,0± 0,1 °C and were found to be practically independent of the concentration of quencher, showing that the viscosity plays no part in changing the degree of polarization of fluorescence with the concentration of quencher.

The degree of polarization of fluorescence obtained by measurement (p') was corrected for secondary luminescence using the equation

$$p = \frac{p'}{1 - \varkappa(1 - 0{,}6p')}$$

given in [11], where p denotes the true degree of polarization and $\varkappa (\equiv S/P$, the ratio of the intensities of secondary and primary luminescences) is a quantity given in [12] as a function of the exciting wavelength, the wavelength of observation, and the yield of fluorescence. The spectra for calculating $\varkappa$ were determined by means of a photoelectric spectrophotometer (Optica Milano CF-4).

2. The systems investigated were fluorescein dissolved in NaOH of pH = 12,5 in a concentration of $2{,}5 \cdot 10^{-4}$ mole/l and quenched with KI, trypaflavine dissolved in ethanol containing $3 \cdot 10^{-3}$ mole/l acetic acid in a concentration of $1 \cdot 10^{-3}$ mole/l and quenched with hydrochinone.

The absorption spectra of all solutions were found to be independent of the concentration of quencher in accordance with earlier statements [13] for the case of fluorescein.

Discussion

1. As the absorption and emission spectra of the solutions do not change, the degree of polarization of fluorescence however, increases with the increase of the concentration of quencher, the quenching may be either of dynamic or mixed type. In order to decide which mechanism is to be made responsible for the quenching, the slope of the function $1/p = f(\eta/\eta_0)$ is to be examined. In [14] η/η_0 is given as a function of the concentration of quencher for fluorescein solutions, in [15] this value is given for trypaflavine solutions. Making use of these data $1/p$ is represented as a function of η/η_0 in Fig. 2. The function $1/p = f(\eta/\eta_0)$ is linear in both cases, thus the quenching is of dynamic type in the studied range of concentration of dyestuff and Eq. (4) is valid for both systems. This means, further that, though conclusions based on the nonlinearity in case of fluorescein (see [1], [7] and [9]) may, in general, be acceptable, they are not reliable for the case in question.

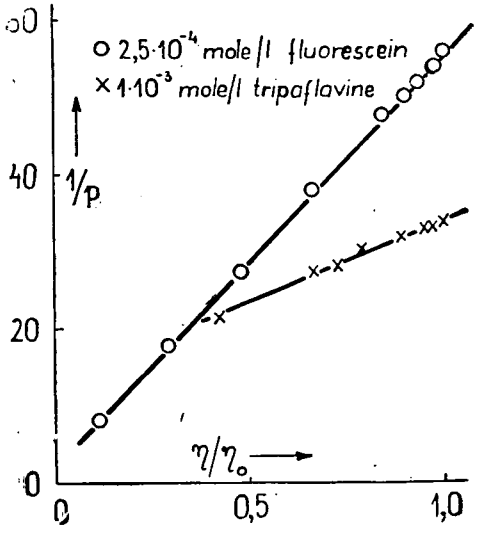

Fig. 2

2. Several papers dealing with the connection of luminescence of solutions and the dielectric relaxation of solvent [17] were recently published. As the dipole moment of an excited luminescent particle differs from that of an unexcited one, a rearrangement of the solvent molecules around a solute particle should take place when the latter goes over to the excited state. During this rearrangement, however, not only the solvent but also the solute particles should rotate. The rotation of the solute particles results in a rotational depolarization of fluorescence. The dielectric relaxation time of the solvent may be given by the DEBYE equation

$$\tau' = \frac{4\pi r'^3 \eta_v}{kT} = \frac{3V'\eta_v}{kT}, \qquad (5)$$

which on substituting into Eq. (2) leads to the relation

$$\frac{1}{p}-\frac{1}{3}=\left(\frac{1}{p_\infty}-\frac{1}{3}\right)\left(1+3\frac{V'}{V}\frac{\tau}{\tau'}\right), \tag{6}$$

where $V=4\pi r^3/3$ and $V'=4\pi r'^3/3$ are the volumes of the solute and solvent particles (considered as spheres). If $\tau/\tau_0=\eta/\eta_0$ then

$$\frac{1}{p}-\frac{1}{3}=\left(\frac{1}{p_\infty}-\frac{1}{3}\right)\left(1+3\frac{V'}{V}\frac{\tau_0}{\tau'}\frac{\eta}{\eta_0}\right). \tag{7}$$

In case of the function $1/p=f(\eta/\eta_0)$ being linear, the constant $V'\tau_0/V\tau'$ can be obtained by experiment. It is to be noted that the validity of Eq. (6) is restricted to cases in which Eq. (5) holds, *i. e.* — among others — V' must be very small compared to V[1].

In [14] it has been shown that the concentration dependence of the relative yield (at least for the case of fluorescein dissolved in water and quenched with KI) can be given by the JABŁOŃSKI-equation

$$\frac{\eta}{\eta_0}=\frac{1-e^{-v}}{v}=\frac{1-e^{-N'vc_q}}{N'vc_q}, \tag{8}$$

where $N'=6{,}02\cdot10^{20}$ and v (the volume of an effective sphere) is an empirical constant. On putting (8) into Eq. (7) we obtain a connection between the degree of polarization of fluorescence (p) and the concentration of quencher (c_q):

$$\frac{1}{p}-\frac{1}{3}=\left(\frac{1}{p_\infty}-\frac{1}{3}\right)\left(1+3\frac{V'}{V}\frac{\tau_0}{\tau'}\cdot\frac{1-e^{-N'vc_q}}{N'vc_q}\right). \tag{9}$$

As Fig. 3 shows, the theoretical curves calculated by Eq. (9) and drawn by solid line it can be fitted to the experimental points fairly well. Curves (*a*) and (*b*) represent the values for fluorescein and trypaflavine respectively. In case of fluorescein the following data were used for calculating $p_\infty/p=2{,}748$; $V'\tau_0/V\tau'=7{,}6$; $v=2{,}94\cdot10^{-20}\,\mathrm{cm}^3$ (after [14]). According to fluorometric measurements $\tau_0=4{,}0\cdot10^{-9}\,\mathrm{s}$ [19]; the radius of the water molecule $r'=1{,}36\,\text{Å}$ (from [20], p. 88), thus $V'=10{,}53\cdot10^{-24}\,\mathrm{cm}^3$; the volume of the fluorescein anion (including its hydrate envelope) $V=58{,}9\cdot10^{-23}\,\mathrm{cm}^3$ (from a molar volume of 480 cm^3 given in [16]). These data give a dielectric relaxation time $\tau'=0{,}99\cdot10^{-11}\,\mathrm{s}$ for water. According to [21] (p. 384) $\tau'=0{,}96\cdot10^{-11}\,\mathrm{s}$ can be obtained by direct measurement of dielectric relaxation time. This value is in a very good agreement with that obtained by the measurement of degree of polarization of fluorescence[2].

In case of trypaflavine $V'\tau_0/V\tau'=1\cdot18$ and $v=0{,}76\cdot10^{-20}\,\mathrm{cm}^3$ [15]. In [16] the molar volume of trypaflavine in ethanol with its solvate envelope is given to be

[1] In [18] similar considerations leading to an equation like Eq. (6) are given, though the conclusions drawn are somewhat different.

[2] The value of the molar volume of flurescein is 247 cm^3 without hydratation; using this value we obtain for $\tau'=1{,}9\cdot10^{-11}\,\mathrm{s}$ which differs from $0{,}96\cdot10^{-11}\,\mathrm{s}$ to a high extent. It seems obvious, that in this phenomenon the solute particle must be taken into account together with its solvent envelope.

about 970 cm^3. According to this value $V = 1{,}20 \cdot 10^{-21}$ $cm^3 \cdot V' = 7{,}19 \cdot 10^{-23}$ cm^3 (calculated from the molar weight and density of ethanol), $\tau_0 = 4{,}0 \cdot 10^{-9}$ s [19]. For the dielectric relaxation time of ethanol we obtain a value of $\tau' = 20{,}3 \cdot 10^{-11}$ s.

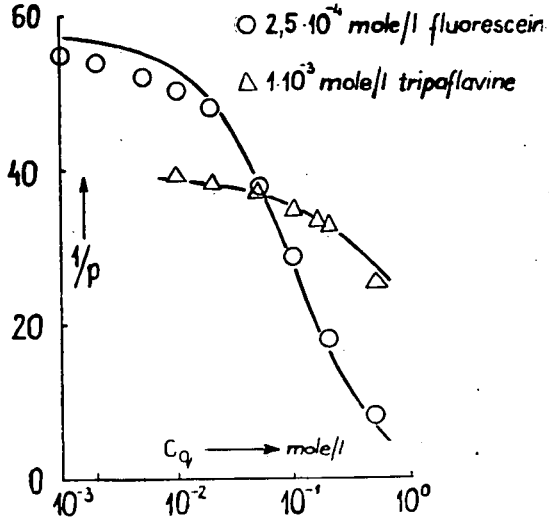

Fig. 3

In [21] (p. 348) $\tau' = 14{,}4 \cdot 10^{-11}$ s is given from direct measurements. The agreement of these two values is not so good as that of the values for fluorescein, but considering the uncertain values of the volumes used for the calculation of τ' a better agreement may hardly be expected. In any case it would be very interesting to investigate further systems, especially of a type in which the DEBYE-equation surely does not hold. For us it seems very probable that even in these systems the dielectric relaxation time — as local characteristic of solvent — plays a deciding role in rotational depolarization, in which case, not the macroscopic, but the local viscosity is known to be important.

* * *

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ИССЛЕДОВАНИЯ О СВЯЗИ СТЕПЕНЬ ПОЛЯРИЗАЦИИ И ТУШЕНИЯ ПОСТОРОННЕГО ВЕЩЕСТВА ФЛУОРЕСЦЕНЦИРУЮЩИХ РАСТВОРОВ

Л. Салаи и Л. Соллоши

Потушенних KI-ом растворов флуоресцеина и трипафлавина тушение имеет динамический характер. Для степени поляризации флуоресценции растворов в зависимости от концентрации тушителя дано формула и контролирована экспериментально.

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ИССЛЕДОВАНИЕ ВОЗБУЖДЕННЫХ СОСТОЯНИЙ МОЛЕКУЛ В ПАРАХ С ПОМОЩЬЮ УНИВЕРСАЛЬНОГО СООТНОШЕНИЯ[1]

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(Поступило в редакцию 5-ого декабря, 1963. г.)

Экспериментально исследовалось универсальное соотношение Степанова в случае паров. Из результатов вычисляются колебательная теплоёмкость этих веществ.

Степанов [1] установил, что между спектрами люминесценции и поглощения имеет место универсальное соотношение:

$$\frac{w_\nu}{\varepsilon_\nu} = D\nu^3 e^{-\frac{h\nu}{kT}} \tag{1}$$

или

$$F_\nu = \ln\frac{\varepsilon_\nu}{w_\nu} + 3\ln\nu = \frac{h\nu}{kT} + \text{const}, \tag{1'}$$

где W_ν — мощность люминесценции, ε — коэффициент поглощения, T — температура, h и k — постоянные Планка и Больцмана, D — постоянная, не зависящая от частоты ν. Основным условием, необходимым для выполнения универсального соотношения, является установление равновесного распределения возбужденных молекул до акта испускания. Если универсальное соотношение выполняется, то левая часть равенства (1′) должна быть линейной функцией от ν, а наклон прямой F_ν должен дать температуру возбужденных молекул T. В работах [2–6] было показано, что для растворов функция F_ν строго линейна и найденная из наклона этой прямой температура соответствует опытной.

В случае разреженных паров за время жизни возбужденных молекул в общем не успевает установиться равновесное распределение молекул по колебательным уровням, соответствующее опытной температуре T. Средний запас колебательной энергии возбужденных молекул зависит от частоты возбуждающего излучения ν_B, в результате спектры флуоресценции, квантовый выход и длительность возбужденного состояния оказываются зависящими от ν_B [7–10]. Если однако распределение колебательной энергии по степеням свободы внутри молекул, установившееся при возбуждении данной частотой ν_B, можно характеризовать температурой T^*, то функция F_ν будет линейной, а найденные из наклона этой прямой F_ν температура T^* должна соответствовать температуре возбужденных моле-

[1] Доклад, прочитанный на VII. Европейском Конгрессе по молекулярной спектроскопии

кул. Отклонение функции F_ν от линейной может служить мерой отклонения распределения от равновесного, характеризуемого для данной частоты ν_B температурой T^*.

Нами, по описанной в работах [11, 12] методике определены температуры возбужденных молекул паров веществ со сплошными электронными спектрами (3,6-тетраметилдиамино-, 3-амино- и 3,6-диаминофталимиды, 1-аминоантрахинон и β-нафтиламин) и со спектрами с выраженной колебательной структурой (антрацен, перилен) при возбуждении различными частотами ν_ν.

Для всех изученных веществ найдена частота $\nu_B = \nu_0$, для которой функция F_ν является строго линейной, а найденные из наклона температуры возбужденных молекул T^* соответствуют опытным температурам паров. При возбуждении этой частотой молекулы не изменяют среднего запаса колебательной энергии, сохраняют равновесное распределение, характеризуемое температурой T и, таким образом, эта частота должна соответствовать частоте электронного перехода ν_{el}. Частоты ν_{el} совпали с частотами инверсии, найденными ранее для 3,6-тетраметилдиамино- и 3-аминофталимидов [13] и близки к частотам $0-0$ переходов в структурных спектрах антрацена и перилена [14, 15].

Не останавливаясь на детальных описаниях функций F_ν для различных ν_B отметим лишь, что отклонения от линейности возрастают с удалением ν_B от ν_{el} и быстрее проявляются для веществ со структурными спектрами. Однако эти отклонения не вносят ошибки большей 10% в определении T^*. При возбуждении флуоресценции паров частотами $\nu_B > \nu_{el}$ температуры возбужденных молекул T^* оказались большими опытных температур T, а для $\nu_B < \nu_{el}$, соответственно, $T^* < T$.

На рис. 1 и 2 для иллюстрации приведена зависимость $\Delta T = T^* - T$ от ν_B (кривые 1), соответственно, для паров 3-аминофталимида и антрацена. Из этих рисунков следует, что ΔT при стоксовом возбуждении в пре-

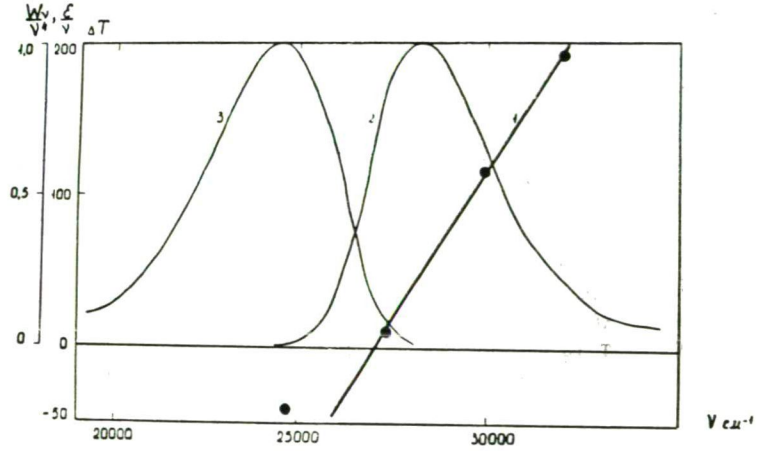

Рис. 1. Зависимость температур возбужденных молекул паров 3-аминофталимида от, частоты возбуждающего излучения при температуре опыта 538 °К: $1 - \Delta T(\nu_B)$, 2 — спектр поглощения, 3 — спектр флуоресценции ($\nu_B = 27290$ см$^{-1}$)

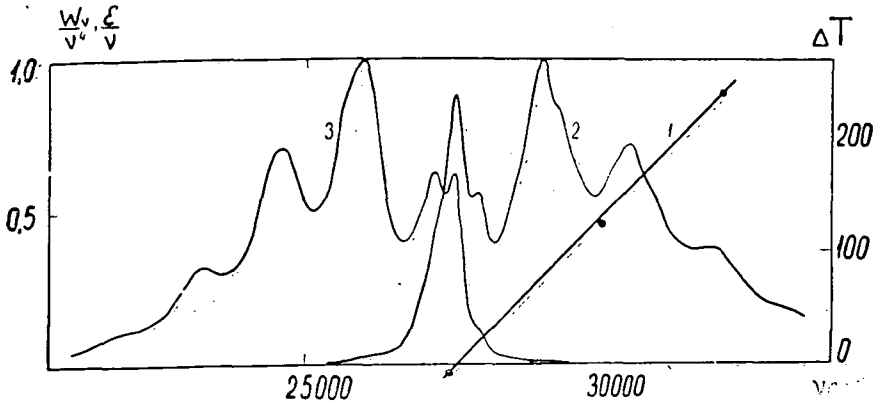

Рис. 2. Зависимость температур возбужденных молекул паров антрацена от частоты возбуждающего излучения при температуре опыта 503 °К: 1 — $\Delta T(\nu_B)$, 2 — спектр поглощения, 3 — спектр флуоресценции ($\nu_B = 27290$ см$^{-1}$).

делах первой полосы полгощения зависит линейно от ν_B, что свидетельствует об эквивалентности оптического и термического способов изменения запаса колебательной энергии молекул паров. Из наклона прямых $\Delta T(\nu_B)$ можно найти колебательные теплоемкости C_{kal} молекул в парах.

В таблице приведены колебательные теплоемкости паров некоторых веществ, найденные по вышеописанному методу — I, найденные по методу Непорента или по зависимости спектров флуоресценции от T и ν_B [9, 16, 17] — II, и рассчитанные теоретически[1] — III. В последнем столбце таблицы указаны опытные температуры паров.

Таблица

	Вещество	Теплоемкости в см$^{-1}$ град$^{-1}$			T°K
		I	II[2]	III	
1.	3,6-тетраметилдиаминофталимид	29,8	21,5	32,5	558
2.	3-аминофталимид	24,9	17	18,4	538
3.	β-нафтиламин	29	24	—	423
4.	Антрацен	18,5	19,5	—	503
5.	Перилен	34	39	—	513

Анализ данных таблицы показывает, что найденные различными методами C_{kal} находятся в удовлетворительном согласии.

В заключение остановимся еще на одном следствии, вытекающем из универсального соотношения. Кечкемети, Домби, Хорваи [5], а затем Ален-

[1] Автор приносит благодарность профессору И. Н. Годневу за расчет теплоемкостей.

[2] Найдены средние C_{kal} в изучавшемся интервале температур.

цев, Пахомычева [18] и Мазуренко [19], изучая выполнимость универсального соотношения в широкой области перекрытия спектров флуоресценции и поглощения растворов, обнаружили для крайней длинноволновой части спектра поглощения значительное нарушение линейности функции F_ν, и показали, что эти отклонения обусловлены наличием невозбуждающего поглощения [16] и их можно количественно связать со спектральной зависимостью антистоксового падения выхода флуоресценции изучаемых растворов.

Нами аналогичные исследования были выполнены для паров 3,6-тетраметилдиамино- и 3-аминофталимидов. Предварительно вещества тщательно очищались. Спектры флуоресценции для $\nu_B = \nu_{el}$, и спектры поглощения паров этих веществ были детально измерены в широкой области перекрытия (4500—5000 $см^{-1}$). На рис. 3 приведены спектры флуоресцен-

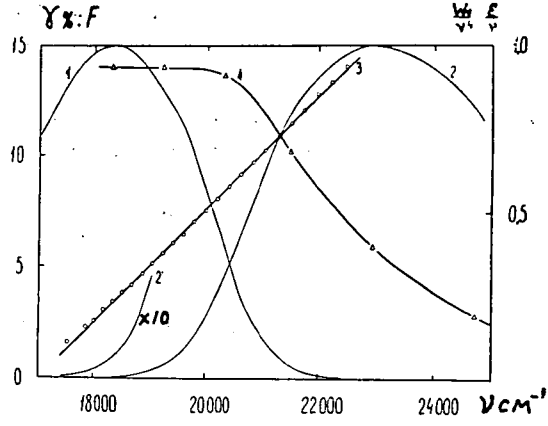

Рис. 3. Спектры флуоресценции (1), поглощения (2 и 2′), функция $F_\nu(3)$ и спектр квантового выхода (4) паров 3,6-тетраметилдиаминофталимида при температуре 558 °К.

ции (кривая 1) и поглощения (кривые 2 и 2′) функция F_ν (кривая 3) и спектр квантового выхода флуоресценции (кривая 4) паров 3,6-тетраметилдиаминофталимида. Из рисунка видно, что функция F_ν линейна во всем изученном спектральном интервале, включая и крайнюю длинноволновую область. Соответственно не имеет места и антистоксово падение выхода паров этого образца. Для исследовавшегося ранее [10] образца этого вещества не такой высокой степени чистоты наблюдались антистоксово падение выхода флуоресценции паров и соответственно нарушение линейности функции F_ν. Аналогичные результаты получены для паров 3-аминофталимида. Этот же тщательно очищенный образец 3-аминофталимида затем был изучен в растворе. Если принять необходимые предосторожности от загрязнения раствора во время эксперимента, то удается получить линейную функцию F_ν в области, в которой наблюдалось [19] заметные отступления от универсального соотношения и падение выхода. Таким образом, невозбуждаю-

щее поглощение связано с наличием посторонних примесей, и для чистых веществ как в парах, так и в растворах не должно наблюдаться антистоксового падения квантового выхода флуоресценции.

INVESTIGATION OF EXCITED STATES OF VAPOUR MOLECULES BY HELP OF GENERAL RELATIONS

N. A. Borisevich

The validity of STEPANOV's equation was experimentally investigated in the case of vapours. The results were used to calculate the vibrational specific heat of the substance.

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ÜBER EINEN ANALYTISCHEN AUSDRUCK FÜR ABSORPTIONS- UND FLUORESZENZSPEKTREN VON LÖSUNGEN

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(Eingegangen am 2. Januar 1964)

Es wurde nachgewiesen, daß die Form der Absorptions- und Emissionsspektren von fluoreszierenden Farbstofflösungen mit einer verhältnismäßig einfachen Formel zu beschreiben ist. Aus den Untersuchungen geht hervor, daß die Frequenz des reinen Elektronenüberganges sowohl aus dem Absorptions-, als auch dem Emissionsspektrum mit hinreichender Genauigkeit bestimmt werden kann.

§ 1. Es wurde bereits von mehreren Autoren versucht, die Gestalt der kontinuierlichen Lichtabsorptions- und Fluoreszenzemissionsspektren von verwickelten mehratomigen Molekülen zu deuten [1]. Bei solchen Untersuchungen werden die absorbierenden bzw. emittierenden Moleküle im allgemeinen durch möglichst einfache Modelle ersetzt und es wird versucht, die Energieverteilung der Moleküle, sowie den Verlauf der Spektren durch Formeln anzunähern, in denen bloß eine geringe Anzahl von Parametern verwendet wird, die mit den zu Grunde gelegten Modellen in Verbindung gebracht werden können. Derartige Näherungsrechnungen sind aber im Falle von vielatomigen Molekülen in gelöstem Zustand nur in geringem Maße geeignet, über die Struktur der Moleküle Aufklärung zu geben. Die Gestalt der Absorptions- und Emissionsspektren der Farbstofflösungen ist nämlich von der chemischen Zusammensetzung der gelösten Stoffe nur wenig abhängig, bloß die Frequenz des reinen Elektronenüberganges wird von der Art und Beschaffenheit des gelösten Stoffes in bedeutenderem Maße beeinflußt. Deshalb schien es uns angebracht, mittels nicht auf Modelle, sondern auf allgemeiner gültige Gesetze bzw. Gesetzmäßigkeiten gegründete Erwägungen analytische Ausdrücke zu finden und zu untersuchen, die möglichst wenige empirische Parameter enthalten, und den Verlauf sowohl der Absorptions- als auch der Emissionsspektren gut wiedergeben, was besonders in dem hinsichtlich der Deutung der Energieübergabe mit und ohne Strahlung so wichtigen Überlappungsgebiete der Spektren der fluoreszierenden Lösungen von Bedeutung ist.

§ 2. Zur analytischen Wiedergabe des Verlaufes der Spektren von verwickelten Molekülen scheint es am geeignetsten, von den beiden Zusammenhängen zwischen den Absorptions- und Emissionsspektren auszugehen, die sich bei fluoreszierenden Lösungen in der Mehrzahl der Fälle — wenigstens in guter Annäherung — gültig erwiesen haben. Diese beiden Beziehungen sind *a)* die wohlbekannte und genauer von BLOCHINZEW formulierte (ursprünglich von LEWSCHIN angegebene) Spiegel-

symmetrierelation [2], und *b)* die modifizierte STEPANOWsche Beziehung [3]. Was die BLOCHINZEWsche Relation betrifft, kann auf Grund unserer Untersuchungen [3] über die STEPANOWsche Beziehung gesagt werden, daß auch die Spiegelsymmetrierelation zu modifizieren ist. Die richtige Relation gibt nämlich nicht den Zusammenhang zwischen der Verteilung $f_q(\nu)$ der Fluoreszenz in Abhängigkeit der Frequenz und dem Absorptionsspektrum $k(\nu)$ wieder, sondern einen Zusammenhang zwischen $f_q(\nu)$ und dem Spektrum der sogenannten aktiven Absorption $k_{akt}(\nu)=k(\nu)\eta(\nu)$, wo $\eta(\nu)$ die Quantenausbeute der Lösung als Funktion der Frequenz des Erregungslichtes bedeutet. Aus der so modifizierten Spiegelsymmetrierelation

$$\frac{f_q(\nu)}{\nu^3} = \text{const}\,\frac{k_{akt}(2\nu_0-\nu)}{\nu} \tag{1}$$

(ν_0 bezeichnet die Spiegelfrequenz) und der modifizierten STEPANOWschen Beziehung

$$f_q(\nu) = \text{const}\,k_{akt}(\nu)\nu^2 e^{-\frac{h\nu}{kT}} \tag{2}$$

ergibt sich, daß das Spektrum der aktiven Absorption in folgender Weise geschrieben werden kann:

$$k_{akt}(\nu) = A\nu e^{\frac{h\nu}{2kT}}\varphi(\nu), \tag{3}$$

während das Emissionsspektrum sich wie folgt schreiben läßt:

$$f_q(\nu) = B\nu^3 e^{-\frac{h\nu}{2kT}}\varphi(\nu) \tag{4}$$

(vgl. [4]). Ferner ist auch leicht einzusehen, daß die in den Gleichungen auftretende Funktion $\varphi(\nu)$ bezüglich der Spiegelfrequenz ν_0 symmetrisch sein muß.

§ 3. Im Verlaufe der gegenwärtigen Untersuchungen versuchten wir die analytische Form der Funktion $\varphi(\nu)$ und zugleich auch diejenige der Absorptions- und Emissionsspektren derart zu bestimmen, daß die Funktion $\varphi(\nu)$ bei Kenntnis der experimentellen Absorptions- und Emissionsspektren einiger organischer Farbstoffe berechnet und dann durch eine einfache analytische Funktion angenähert wurde.

Aus den Gleichungen (3) und (4) ist ersichtlich, daß die Funktion $\varphi(\nu)$ sowohl aus dem Absorptionsspektrum, als auch aus dem Emissionsspektrum bestimmt werden kann. Wird die Untersuchung von $\varphi(\nu)$ auf Grund der Gleichung (3) durchgeführt, so ist außer dem Absorptionsspektrum auch die Ausbeutefunktion $\eta(\nu)$ experimentell zu bestimmen. Es ist zu bemerken, daß — da die Spiegelsymmetrie nie genau erfüllt ist — die aus Gl. (3) bzw. (4) berechneten Funktionen $\varphi(\nu)$ voneinander mehr oder weniger abweichen.

In Abb. 1 wurde der Logarithmus der auf Grund des aktiven Absorptionsspektrums einer Fluoreszeinlösung der Konzentration 10^{-4} Mol/l berechneten Funktion $\varphi(\nu)$ (Kurve 1) dargestellt. Zum Vergleich zeigt die Kurve 2 den Verlauf der auf dieselbe Lösung bezüglichen Funktion $\varphi(\nu)$, bei deren Berechnung aus Gl. (3) $k_{akt}(\nu)$ durch $k(\nu)$ ersetzt wurde. In letzterem Falle, wenn also der spektrale Verlauf von $\eta(\nu)$ außer Acht gelassen wird, weicht die Gestalt der $\varphi(\nu)$ Kurve — wie aus der Abbildung ersichtlich — von der symmetrischen stark ab; dagegen zeigt die aus dem Spektrum der aktiven Absorption berechnete Funktion $\varphi(\nu)$ einen symmetrischen Verlauf.

Die Maximumstelle der auf die genannte Fluoreszeinlösung bezüglichen Funktion $\varphi(\nu)$ (Abb. 1, Kurve 1) ist $\nu_0' = 600 \cdot 10^{12}$ Hz; die Frequenz des reinen Elektronenüberganges ergibt sich auf Grund der Untersuchung der Spiegelsymmetrie nach Gl. (1) zu $\nu_0 = 598 \cdot 10^{12}$ Hz. Die Abweichung zwischen ν_0' und ν_0 beträgt demnach nur 0,3%. Die Maximumstelle der Kurve 2 stimmt praktisch mit derjenigen der Kurve 1 überein, auch falls die Temperatur von 25 °C auf 50 °C geändert wird. Ähnliche Ergebnisse wurden auch mit Aluminium-Morin, Trypaflavin, Rhodulin Orange, Rhodamin B und Eosin erhalten (Abb. 2). Bei der Berechnung der in Abb. 2 dargestellten Funktionen $\varphi(\nu)$ wurden die von uns experimentell bestimmten Funktionen $\eta(\nu)$ berücksichtigt.

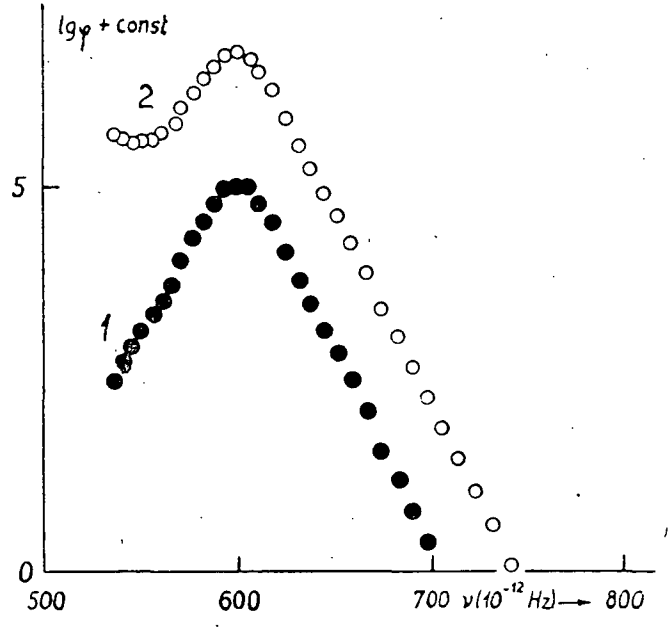

Abb. 1

Auf diese Weise kann also die Frequenz ν_0 des reinen Elektronenüberganges auch aus dem Absorptionsspektrum allein bestimmt werden.

Die auf Grund der Emissionsspektren der verschiedenen Lösungen mit Gl. (4) berechneten Funktionen $\varphi(\nu)$ zeigt Abb. 3 für Aesculin, Aluminium-Morin, Trypaflavin, Fluoreszein, Rhodulin Orange, Eosin, Rose bengale und Rhodamin B. Die Maximumstellen dieser Funktionen $\varphi(\nu)$ stimmen mit den Spiegelfrequenzen der betreffenden Lösungen ebenfalls mit einer maximalen Abweichung von 1% überein. Aus den logarithmisch dargestellten Diagrammen der Abbildungen (2) und (3) ist ersichtlich, daß die einzelnen Kurvenzweige mit wachsender Entfernung von der Maximumstelle immer mehr durch Geraden angenähert werden können, woraus folgt, daß die einen nahezu symmetrischen Verlauf aufweisenden Funktionen $\varphi(\nu)$ in der Form $\varphi(\nu) = \text{const. sech}\,[a(\nu - \nu_0)]$ ausgedrückt werden können. Bei Anwendung

dieser Annäherung *lassen sich die Absorptions- bzw. die Emissionsspektren durch die Formeln*

$$k_{akt}(\nu) = A\nu e^{b\nu} \operatorname{sech}\,[a(\nu_0 - \nu)] \tag{5}$$

bzw.

$$f_q(\nu) = B\nu^3 e^{-b\nu} \operatorname{sech}\,[a(\nu - \nu_0)] \tag{6}$$

darstellen, worin $b = h/2kT$ ist.

Im Verlaufe unserer Untersuchungen wurde zuerst die Erfüllung der Beziehung (6) geprüft. Aus den Ergebnissen der Berechnungen konnte die folgende Folgerung

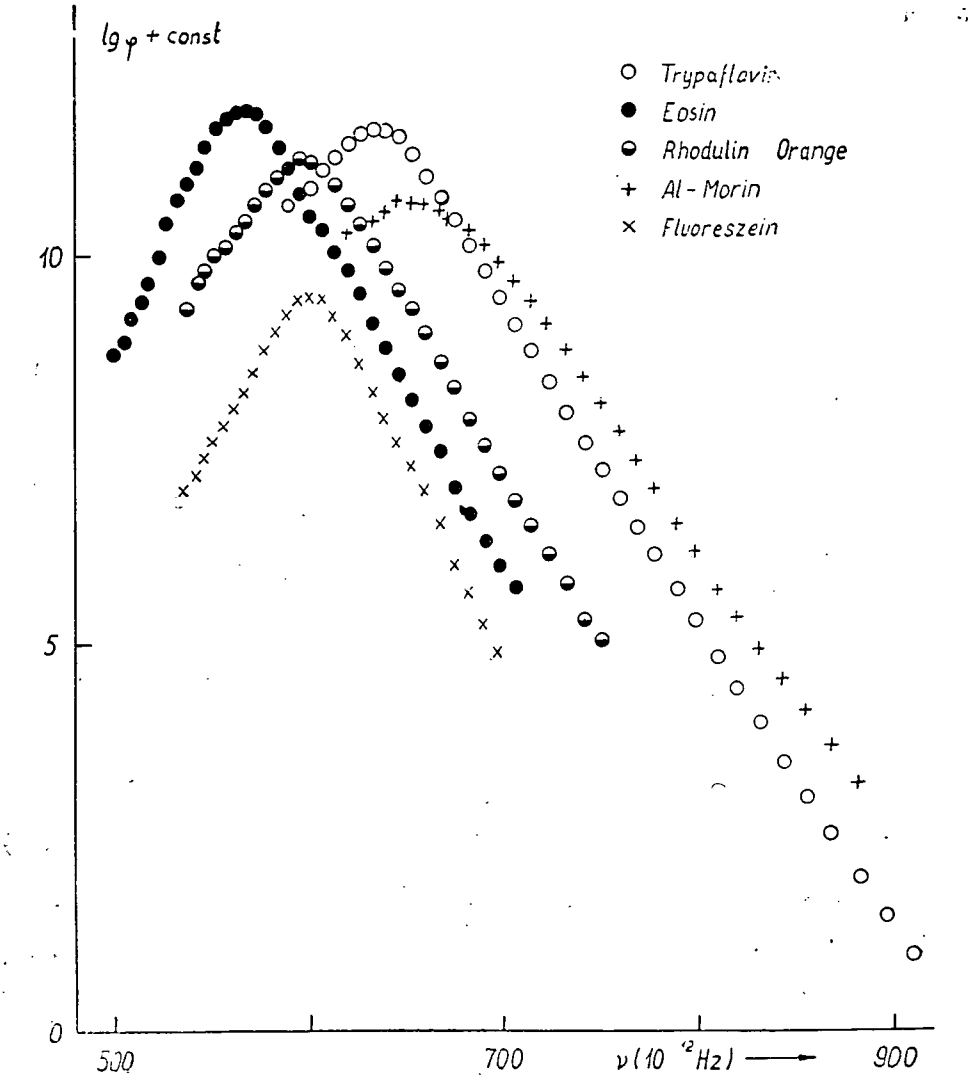

Abb. 2

gezogen werden: Wird in Gl. (6) die absolute Temperatur T der Lösung durch eine ihr nahestehende „effektive Temperatur T^* der Moleküle" ersetzt, so wird bei entsprechender Wahl des Parameters a der Verlauf des Emissionsspektrums durch Gl. (6) befriedigend wiedergegeben[1]. Als Beispiel wird in Abb. 4 für Rhodamin B, Fluoreszein und Trypaflavin gezeigt, wie weit die nach (6) berechneten Spektren die gemessenen annähern. Die Kurven der Abbildung stellen die mit den dort angegebenen Parameterwerten berechneten Spektren dar, neben denen die betreffenden Meßpunkte eingezeichnet sind.

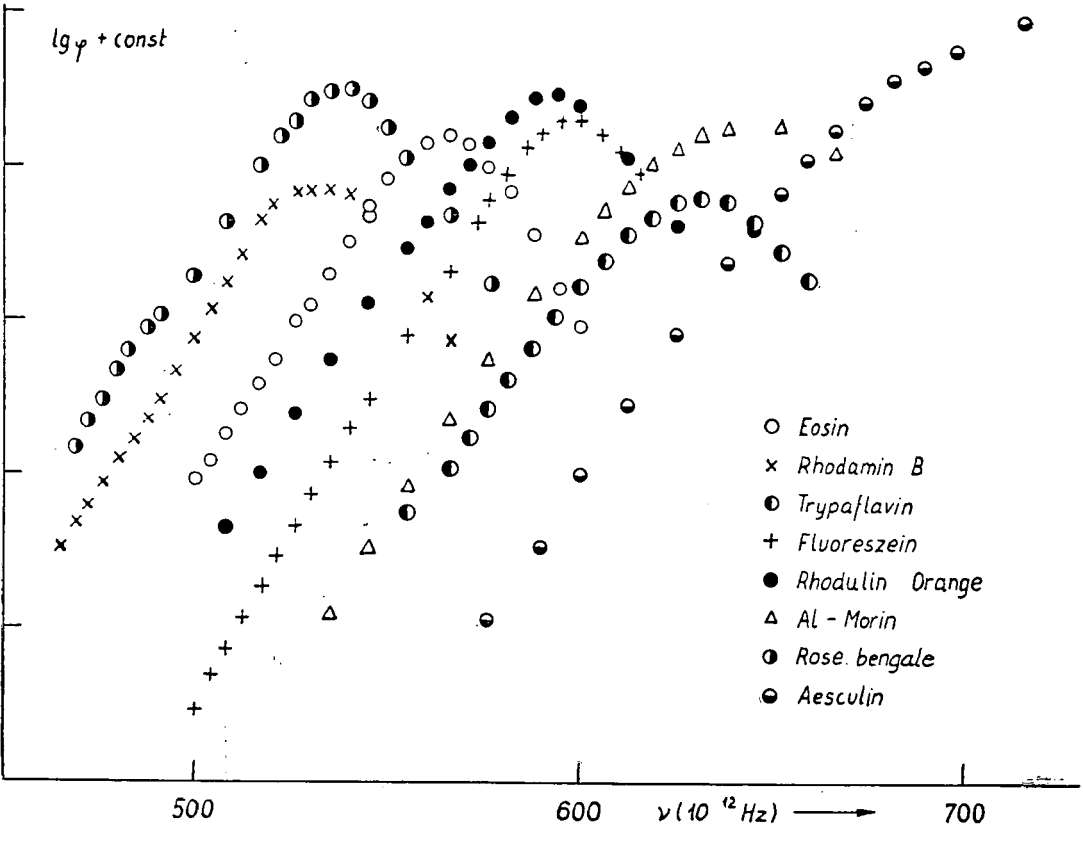

Abb. 3

Zur Prüfung der Genauigkeit der auf die Absorptionsspektren bezüglichen Formel (5) wurden in Abb. 5 die berechneten und die gemessenen Absorptionsspektren der letzterwähnten drei Stoffe dargestellt.

[1] Im Falle dem Spiegelsymmetriegesetz weniger genau genügender Lösungen weichen die berechneten und gemessenen Spektren mit wachsender Entfernung von ν_0 immer stärker voneinander ab.

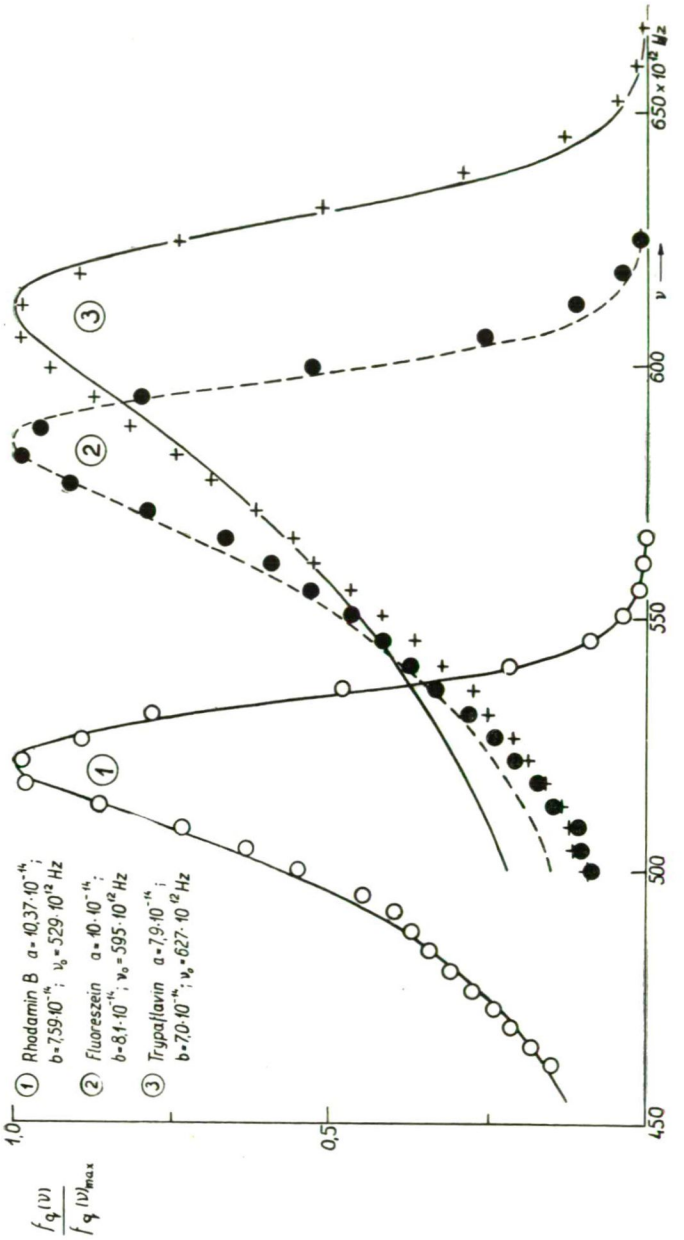
1,0
0,5
4,50
500
550
600
650 × 10¹² Hz
ν
$\frac{f_q(\nu)}{f_q(\nu)_{max}}$
① Rhodamin B a = 10,37·10⁻¹⁴; b = 7,59·10⁻¹⁴; ν₀ = 529·10¹² Hz
② Fluoreszein a = 10·10⁻¹⁴; b = 8,1·10⁻¹⁴; ν₀ = 595·10¹² Hz
③ Trypaflavin a = 7,9·10⁻¹⁴; b = 7,0·10⁻¹⁴; ν₀ = 627·10¹² Hz

Abb. 4

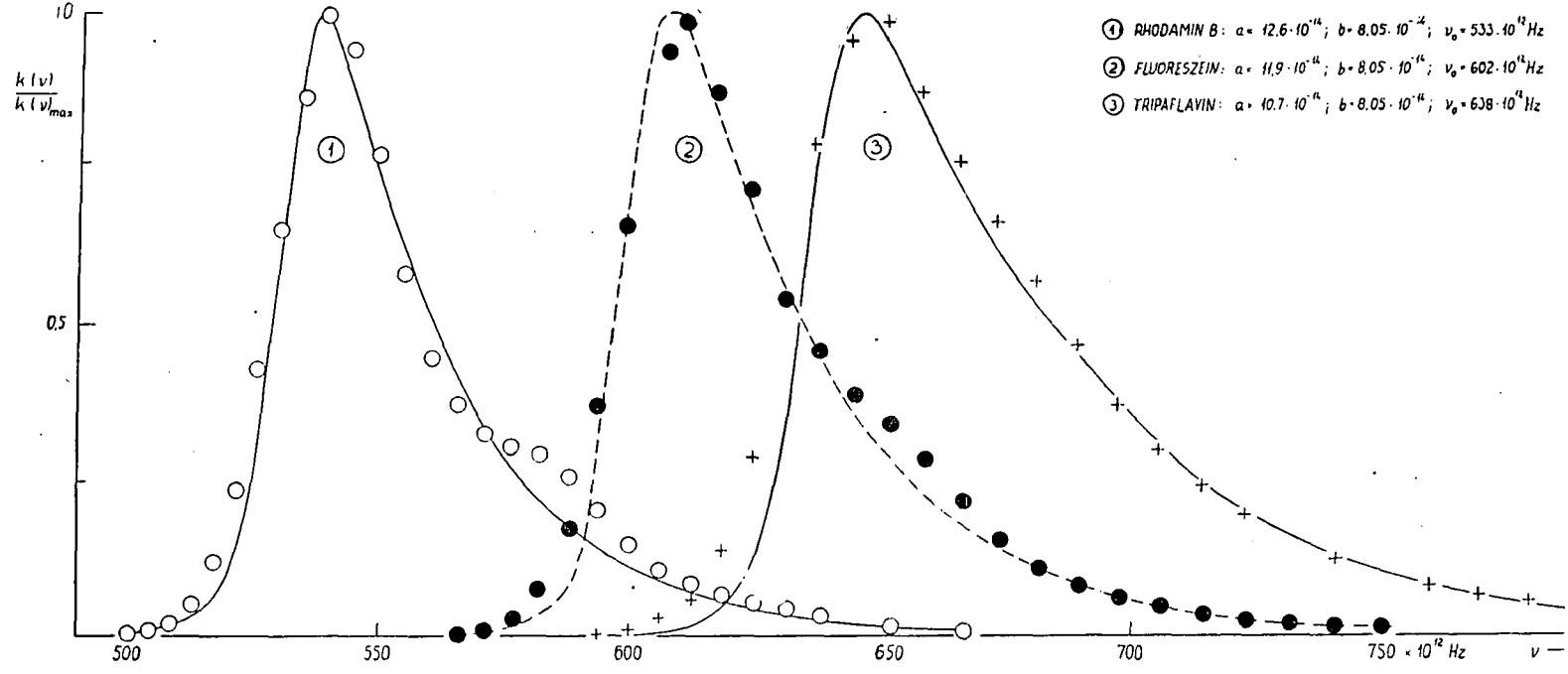
1,0
0,5
k (ν) / k (ν)max
500
550
600
650
700
750 · 10^12 Hz
ν
① RHODAMIN B: a = 12,6 · 10^-14; b = 8,05 · 10^-26; ν0 = 533 · 10^12 Hz
② FLUORESZEIN: a = 11,9 · 10^-14; b = 8,05 · 10^-14; ν0 = 602 · 10^12 Hz
③ TRIPAFLAVIN: a = 10,7 · 10^-14; b = 8,05 · 10^-14; ν0 = 638 · 10^12 Hz

Abb. 5

Aus den Abbildungen 4 und 5 geht hervor, daß sowohl die Absorptions-, als auch die Emissionsspektren der einzelnen Stoffe sich mit Hilfe von verhältnismäßig wenig voneinander abweichenden Parametern annähern lassen; die Übereinstimmung der berechneten und der gemessenen Spektren ist im Falle des Fluoreszeins am besten.

* * *

Verfasser haben Herrn Prof. Dr. A. BUDÓ, Direktor des Institutes für Experimentalphysik der Universität Szeged, für sein ständiges Interesse und seine wertvollen Ratschläge aufrichtig zu danken.

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О АНАЛИТИЧЕСКОМ СООТНОШЕНИИ СПЕКТРОВ ПОГЛОЩЕНИЯ И ИЗЛУЧЕНИЯ РАСТВОРОВ

Й. Домби, И. Кечкемети и *Л. Козма*

Показано, что спектры поглощения и излучения флуоресцирующих растворов можно описать сравнительно простыми формулами. Из исследованиях видно, что частоту чисто электронного перехода можно определить или из спектра поглощения или из спектра излучения достаточно точно.

DIE ÄNDERUNG DES PHOTOSTROMES VON DOPPELT DOTIERTEN KADMIUMSULFID-PHOTOLEITERN IN LUFT UND VAKUUM

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(Eingegangen am 10. Januar 1964)

Es wurde das Verhalten von doppelt — mit Kupfer und Chlor — dotierten mikrokristallinen Photoleitern in Luft und Vakuum bei Raumtemperatur untersucht. Nach den Meßergebnissen nahm die Photoleitfähigkeit im untersuchten Wellenlängengebiet ($0{,}3-1\mu$) in trockener und feuchter Luft gegen den Photostrom in Vakuum u. zw. mit großer Trägheit ab, was durch die Gesetzmäßigkeiten der entsprechenden Photostromabnahme in Kadmiumsulfid-Einkristallen zu erklären ist. Die Änderung des Photostromes erwies sich in den untersuchten Fällen als reversibel.

Einleitung

Die Anwendung von einem oder mehreren Zusätzen in verschiedenen Konzentrationen zur Steigerung der Empfindlichkeit von Kadmiumsulfid-Photoleitern kann die Empfindlichkeit in einzelnen Spektralgebieten oder innerhalb des ganzen sichtbaren Gebietes erhöhen [1, 2]; die praktisch größte Wirkung kann im allgemeinen mit Kupfer und Chlor erreicht werden; ihre Wirkung ist bei gleichzeitiger Anwendung besonders stark [3, 4, 5, 6]. Die hohe Empfindlichkeit eines Photoleiters kann aber nur dann voll ausgenützt werden, wenn der Photostrom sich bei konstanter Belichtung nicht erheblich ändert. Unter den Ursachen der Änderung des Photostromes bei konstanter Belichtung kann die durch die umgebende Atmosphäre hervorgerufene Änderung eine Rolle spielen; diese kann — wenn es nötig erscheint — durch den Einbau des Photoleiters in eine Schutzatmosphäre vermieden werden.

Der Zweck gegenwärtiger Arbeit war, bezüglich der Änderung des spektralen Verlaufes des Photostromes bei hochempfindlichen, mit Kupfer und Chlor doppelt dotierten Kadmiumsulfid-Photoleitern Daten zu liefern. Nach früheren Untersuchungen [7, 8, 9] wird die Stärke und die spektrale Verteilung des Photostromes in Kadmiumsulfid-Einkristallen durch Wasserdampf und Sauerstoff stark beeinflußt. Deshalb war der Gegenstand unserer Untersuchungen die Änderung des Photostromes in mit Kupfer und Chlor von verschiedenen Konzentrationen doppelt dotierten mikrokristallinen Kadmiumsulfid-Photoleitern in trockener und mit Wasserdampf gesättigter Luft bei Raumtemperatur, gegenüber dem in Vakuum gemessenen Photostrom.

Experimentelles

Bei der Herstellung des mikrokristallinen Kadmiumsulfid-Photoleiters wurde das einen Kadmiumüberschuß aufweisende Kadmiumsulfid-Pulver zuerst mit Kupfer dotiert und bei etwa 600 °C ausgeglüht; nach Auswaschen wurde dann Chlor zugegeben und das Pulver nach Trocknen wieder einer Wärmebehandlung bei etwa 600 °C unterworfen. Die doppelte Dotierung bestand aus allen möglichen Kombinationen von 0,2, 0,4, 0,8 Gew.-‰ Kupfer und 1,5, 3, 6 Gew.-‰ Chlor. Aus den so erhaltenen Pulvern wurden mit einem Druck von 10 000 kp cm^{-2} 0,7 mm dicke scheibenförmige Tabletten von 14 mm Durchmesser gepreßt und dann bei etwa 600 °C wieder kurz ausgeglüht. Auf die so hergestellten Tabletten wurden in Hochvakuum kammförmige Indiumelektroden aufgedampft, endlich wurden sie mit Kontaktelektroden aus einer Gallium-Zinn-Legierung versehen. Die wirksame Fläche des Photoleiters war etwa 0,4 cm^2.

Zur Belichtung des Photoleiters diente das spektral zerlegte Licht einer Osram Xenonlampe Typ. XBO 162 von 133 Watt, die mit einem Zeiss-schen Spiegelmonochromator mit Quarzoptik und einer Spaltbreite von 0,1 mm erzeugt wurde. Da die spektrale Verteilung des Photostromes davon abhängt, ob die Messung bei den kleineren oder den größeren Wellenlängen beginnt [10, 11], wurden die Messungen in Abständen von je 10 $m\mu$ in beiden Richtungen durchgeführt; in der Meßkurve sind die Mittelwerte beider Messungen aufgetragen. Die spektrale Verteilung des Photostromes wurde im Intervall von $0{,}3-1\,\mu$ untersucht. Die gemessenen Photoströme wurden auf gleiche Belichtungsenergien umgerechnet; als Bezugsgröße diente die Stromstärke bei 550 $m\mu$. Während der Messungen war auf den Photoleiter eine Gleichspannung von 50 Volt geschaltet, was einer Feldstärke von etwa 200 V cm^{-1} entspricht. Während sämtlicher Messungen befand sich der Photoleiter in demselben, mit einem Quarzfenster versehenen Glasgefäß. Das Vakuum von der Größenordnung 10^{-6} Torr wurde mit einer gläsernen Quecksilberdiffusionspumpe hergestellt und mit einem McLeod-Manometer gemessen. Das Eindringen des Quecksilberdampfes zum Präparat wurde durch hintereinander geschaltete, mit flüssiger Luft gekühlte Fallen verhindert. Die Luft wurde mit Phosphorpentoxid getrocknet, zur Sättigung der Luft mit Wasserdampf wurde destilliertes Wasser benützt.

Meßergebnisse und ihre Deutung

Die Figuren 1, 2 und 3 enthalten die bei der Belichtung der 0,2, 0,4 bzw. 0,8 Gew.-‰ Kupfer enthaltenden Kadmiumsulfid-Photoleiter mit spektralzerlegtem Licht in Luft von Raumtemperatur erhaltenen Photoströmen. Die Kurven *a*, *b* und *c* in jeder Figur zeigen den Photostrom eines Photoleiters, der neben der angegebenen Kupferkonzentration noch 1,5, 3 bzw. 6 Gew.-‰ Chlor enthält. Die Stromstärke des Dunkelstromes war zwischen 10^{-6} bis 10^{-11} A in Abhängigkeit von der Zeitdauer und der Temperatur der Wärmebehandlung sowie der Kupfer- und Chlorkonzentration. Auch aus unseren Messungen ergab sich, daß unter sonst gleichen Umständen die Kupferdotierung allein die Dunkel- und Photoleitfähigkeit des Kadmiumsulfids herabsetzte, während der Chlorzusatz dieselbe verstärkte, was mit dem bisherigen Angaben der Literatur übereinstimmt. Da Chlor als Donator, Kupfer dagegen als Akzeptor in das Gitter des Kadmiumsulfids eingebaut werden, können ihre Wirkungen einander — je nach dem Verhältnis ihrer Konzentrationen — sowohl hinsichtlich der Leitfähigkeit, als auch der Photoleitfähigkeit gegenseitig kompensieren, oder auch verstärken. Im Falle einer doppelten Dotierung ist es leichter, das optimale Verhältnis zwischen Photostrom und Dunkelstrom bei gegebener Chlordotierung mit Hilfe der durch die Kupfer- (eventuell auch anderer, z. B. Silber-) Akzeptoren verursachte Abnahme der Stromstärke einzustellen, als mit der Veränderung der Chlorkonzentration allein. Sämtliche Kurven zeigen, den benützten hohen Konzentrationen der doppelten Dotierung entsprechend, mehrere Störstellen-Niveaus in Abhängigkeit von der Höhe und dem gegenseitigen Verhältnis der Verunreinigungskonzentrationen der einzelnen Präparate; für alle ist es charak-

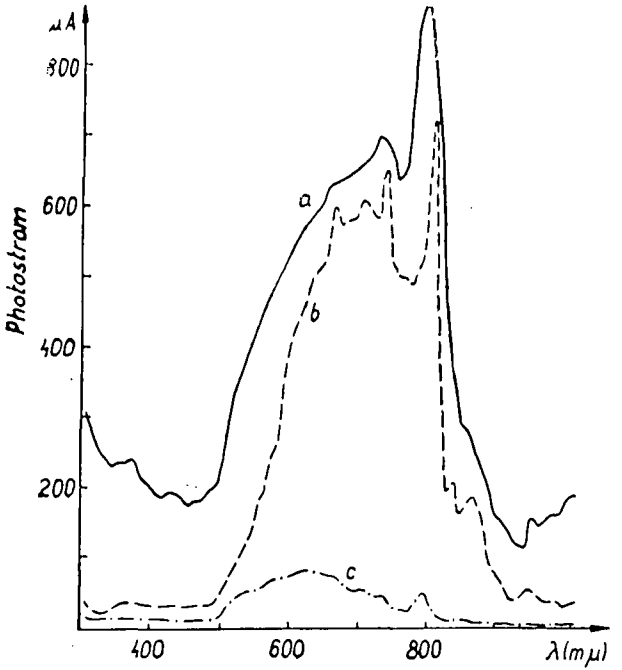

Fig. 1. Spektrale Verteilung des Photostromes von Kadmiumsulfid-Photoleitern, dotiert mit 0,2 Gew.-‰ Kupfer u. 1,5 Gew.-‰ Chlor (Kurve *a*), mit 0,2 Gew.-‰ Kupfer u. 3 Gew.-‰ Chlor (Kurve *b*) und mit 0,2 Gew.-‰ Kupfer u. 6 Gew.-‰ Chlor (Kurve *c*)

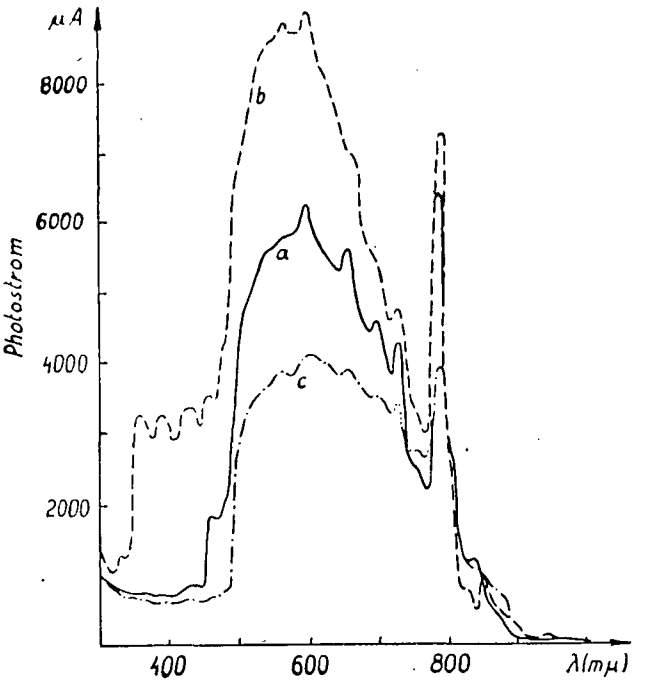

Fig. 2. Spektrale Verteilung des Photostromes von Kadmiumsulfid-Photoleitern, dotiert mit 0,4 Gew.-‰ Kupfer u. 1,5 Gew.-‰ Chlor (Kurve *a*), mit 0,4 Gew.-‰ Kupfer u. 3 Gew.-‰ Chlor (Kurve *b*) und mit 0,4 Gew.-‰ Kupfer u. 6 Gew.-‰ Chlor (Kurve *c*)

teristisch, daß die Maxima der Kurven — in Übereinstimmung mit den Angaben der Literatur — etwa bei 510 mμ, d. h. der Absorptionskante des Kadmiumsulfids beginnen. Aus dem Vergleich der Figuren 1, 2 und 3 geht hervor, daß die mit unserem Verfahren hergestellten Photoleiter bei einer Kupferdotierung von 0,4 Gew.-‰ mit allen benützten Chlorkonzentrationen den höchsten Photostromwert zeigen.

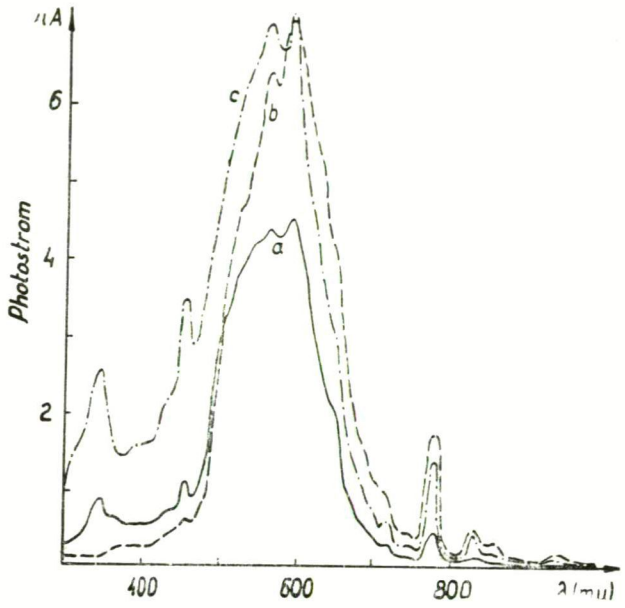

Fig. 3. Spektrale Verteilung des Photostromes von Kadmiumsulfid-Photoleitern, dotiert mit 0,8 Gew.-‰ Kupfer u. 1,5 Gew.-‰ Chlor (Kurve *a*), mit 0,8 Gew.-‰ Kupfer u. 3 Gew.-‰ Chlor (Kurve *b*) und mit 0,8 Gew.-‰ Kupfer u. 6 Gew.-‰ Chlor (Kurve *c*)

Nicht nur die bei einzelnen Wellenlängen gemessenen Werte des Photostromes waren höher als die entsprechenden Werte bei anderen Kupferkonzentrationen, sondern auch die maximalen Werte der Kurven erstreckten sich auf das verhältnismäßig breiteste Intervall. Aus dem Vergleich der Kurven *a*, *b* und *c* in Figur 2 ergibt sich, daß in unseren Versuchen das mit 0,4 Gew.-‰ Kupfer, 3 Gew.-‰ Chlor dotierte mikrokristalline Kadmiumsulfid den maximalen Photostrom lieferte [1, 2, 5, 7, 12, 13].

Figur 4 zeigt die spektrale Verteilung des Photostromes von Kadmiumsulfid-Photoleitern in Vakuum (Kurve *a*), trockener (Kurve *b*) und feuchter Luft (Kurve *c*). Vor Beginn jeder Messung befand sich der Photoleiter eine Stunde lang in der entsprechenden Atmosphäre. Aus der Figur ist ersichtlich, daß auf Einwirkung der Atmosphäre der Photostrom sich im ganzen untersuchten Wellenlängengebiet veränderte, u. zw. derart, daß der Wert des Photostromes in trockener Luft gegenüber dem im Vakuum erhaltenen Werte kleiner war; in feuchter Luft wurde die Verminderung des Photostromes noch stärker als in trockener Luft. Dieses Ergebnis ist mit R. H. BUBES [7] an Kadmiumsulfid-Einkristallen erhaltenen Resultaten nicht

in Einklang, der eine Abnahme des Photostromes auf Einwirkung von feuchter Luft nur bei einer Erregung mit Wellenlängen unter 510mμ nachweisen konnte. Dagegen sind unsere Resultate mit K. W. BÖERS Ergebnissen vereinbar, nach denen nur eine reine Wasserdampfatmosphäre bei der Erregung mit Wellenlängen unter 510mμ den Photostrom in Kadmiumsulfid-Einkristallen herabsetzt, während die ähnliche Wirkung des Sauerstoffs sich auch auf größere Wellenlängen erstreckt.

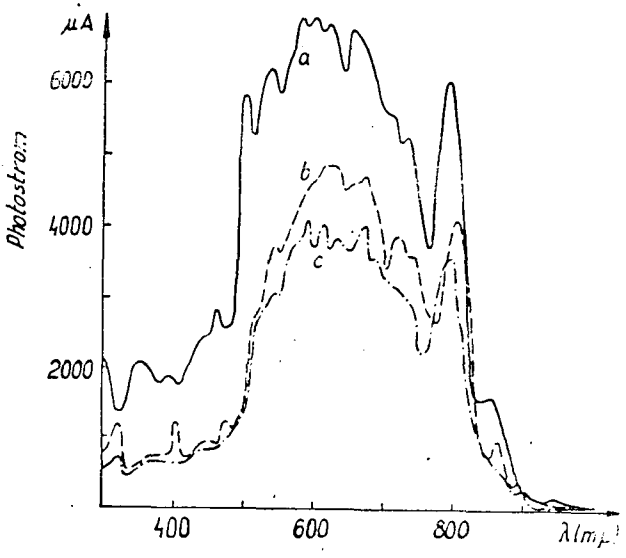

Fig. 4. Spektrale Verteilung des Photostromes von Kadmiumsulfid-Photoleitern in Vakuum (Kurve *a*), trockener Luft (Kurve *b*) und feuchter Luft (Kurve *c*)

In unseren Versuchen zeigt sich in den Wirkungen der trockenen und feuchten Luftatmosphäre auf mikrokristalline Kadmiumsulfid-Photoleiter dieselbe Erscheinung, wie die entsprechende Wirkung der Sauerstoff- und Sauerstoff+Wasserdampf-Atmosphären in K. W. BÖERS Versuchen; dadurch kann die Abnahme des Photostromes im ganzen Wellenlängengebiet in beiden Fällen erklärt werden. Aus der Figur ist ersichtlich, daß die feuchte Luft den in trockener Luft gemessenen Wert des Photostromes nicht so stark herabsetzt, wie die trockene Luft den in Vakuum erhaltenen Wert. Daraus erhellt, daß Sauerstoff eine stärkere Wirkung auf mikrokristallinen Kadmiumsulfid-Photoleiter ausübt, als Wasserdampf, wie es auch bei Kadmiumsulfid-Einkristallen festgestellt wurde [9].

Da es wichtig erschien, die Zeitdauer zu kennen, die zur Erreichung des Endzustandes in verschiedenen Atmosphären nötig ist, wurden auch diesbezügliche Messungen ausgeführt. Die Ergebnisse sind in Figuren 5, 6 und 7 erhalten. Figuren 5 und 6 zeigen, daß — wenn die in Vakuum bzw. in trockener Luft nach einer Stunde gemessenen Photostromwerte als Ausgangspunkt genommen werden — die betreffende Atmosphäre den Photostrom bedeutend ändert, und zwar so, daß nach einer anfänglichen schnellen Änderung die Geschwindigkeit der Änderung ständig abnimmt, so daß der Endzustand erst in etwa zwei Tagen erreicht wird. Die Kurven

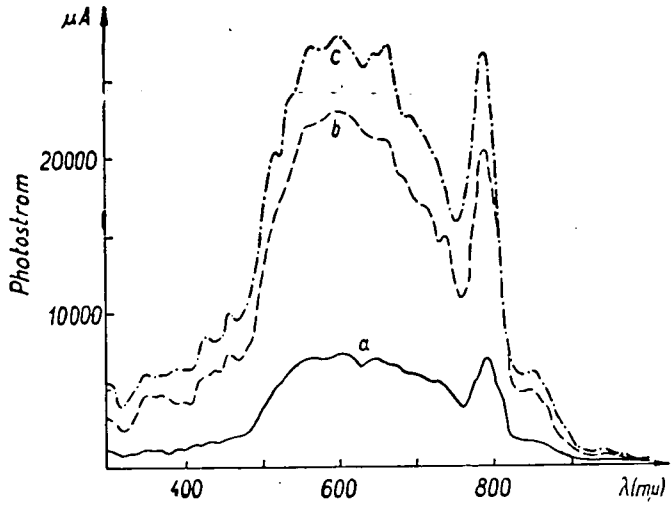

Fig. 5. Spektrale Verteilung des Photostromes von Kadmiumsulfid-Photoleitern in Vakuum nach 1 Stunde (Kurve *a*), nach 6 Stunden (Kurve *b*) und nach 47 Stunden (Kurve *c*)

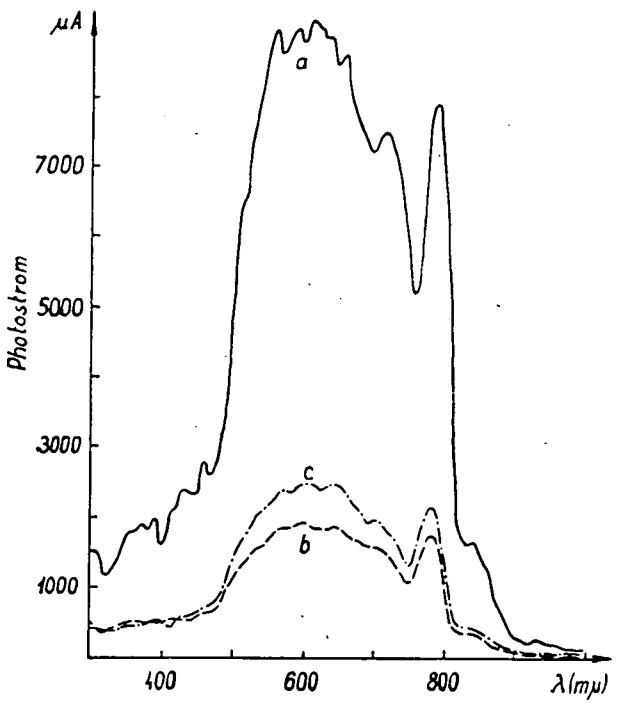

Fig. 6. Spektrale Verteilung des Photostromes von Kadmiumsulfid-Photoleitern in trockener Luft nach 1 Stunde (Kurve *a*), nach 6 Stunden (Kurve *c*) und nach 50 Stunden (Kurve *b*)

der Figur 7 zeigen, daß die Änderung auf Einwirkung der feuchten Luft gleichmäßiger verläuft, aber länger dauert, als in den früher erwähnten Fällen. Noch nach fünf Tagen ist die Abnahme der Stromstärke gut zu messen, was soviel bedeutet, daß der Endzustand in dieser Atmosphäre bei den mikrokristallinen Kadmiumsulfid-Photoleitern nur angenähert wird.

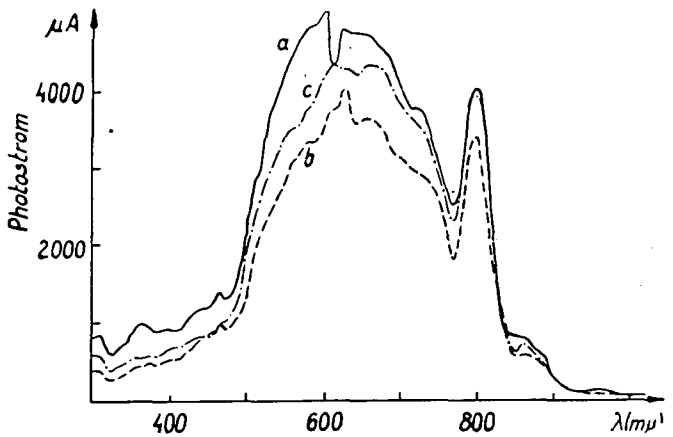

Fig. 7. Spektrale Verteilung des Photostromes von Kadmiumsulfid-Photoleitern in feuchter Luft nach 1 Stunde (Kurve *a*), nach 70 Stunden (Kurve *c*) und nach 120 Stunden (Kurve *b*)

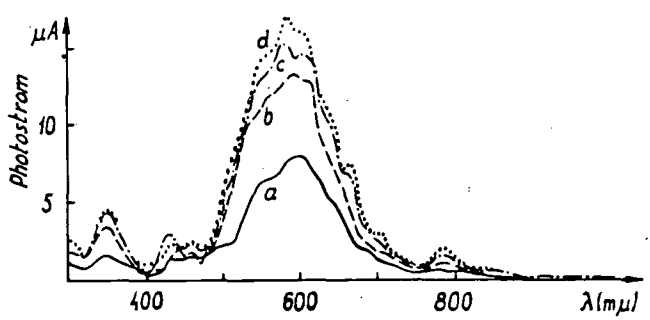

Fig. 8. Spektrale Verteilung des Photostromes von Kadmiumsulfid-Photoleitern mit schwächerer Empfindlichkeit in Vakuum nach 1 Stunde (Kurve *a*), nach 6 Stunden (Kurve *b*), nach 30 Stunden (Kurve *c*) und nach 54 Stunden (Kurve *d*)

Es wurde auch der Charakter der Änderungen untersucht und gefunden, daß sie reversibel sind, d. h. die Ausgangsstromstärke wurde nach entsprechender Zeit in allen Fällen wieder erhalten; die hierzu nötige Zeit ist ungefähr dieselbe, die zur Ausbildung des Endzustandes in den verschiedenen Atmosphären nötig war. Ein Vergleich dieser Ergebnisse mit den an Kadmiumsulfid-Einkristallen erhaltenen Werten zeigt, daß mikrokristallines Kadmiumsulfid eine viel größere Trägheit aufweist, als der Einkristall. Dieses Verhalten des mikrokristallinen Kadmiumsulfids

ist mit der von R. H. BUBE an Kadmiumsulfid-Einkristallen nachgewiesenen Abnahme des Photostromes auf Einwirkung von Wasserdampf in Einklang zu bringen, welche von ihm auf die Zunahme der Oberflächenleitung bzw. der dadurch entstehenden Oberflächenrekombination zurückgeführt wurde [7]. Da die Oberfläche des mikrokristallinen Kadmiumsulfid-Photoleiters verhältnismäßig viel zu größer und verwickelter ist, als diejenige des Einkristalls, ist es zu erwarten, daß die Wirkung des Sauerstoffs und des Wasserdampfs in einer viel komplizierteren Weise zustande kommt, und infolge dessen mit einer größeren Trägheit abläuft. Es wurde das Verhalten der Schichten von höherer und schwächerer Empfindlichkeit mit Rücksicht auf die Verminderung des Stromes durch die Einwirkung der Atmosphäre in den erwähnten drei Fällen untersucht. Die Ergebnisse sind aus dem Vergleich der Fig. 5 und 8 ersichtlich. Fig. 5, die den Photostrom der Kadmiumsulfidschicht von höherer Empfindlichkeit enthält, zeigt, daß diese viel stärker auf die Änderung der Atmosphäre reagiert, als die Schicht von schwächerer Empfindlichkeit, für die die Änderung des Photostromes in Fig. 8 angegeben ist. Dieses Ergebnis stimmt mit den an Kadmiumsulfid-Einkristallen gefundenen diesbezüglichen Resultaten überein [9]. Aus dem Vergleich der beiden Figuren ergibt sich auch, daß die Änderung der weniger empfindlichen Schicht gleichmäßiger ist und länger dauert.

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ИЗМЕНЕНИЕ ФОТОТОКА ДВОЙНО ЗАГРЯЗНЕННЫХ ФОТОПРОВОДОВ СУЛЬФИДА КАДМИЯ В ОБЫКНОВЕННОЙ АТМОСФЕРЕ

Л. Гомбаи, Я. Ланг и Й. Кишпетер

Было исследовано поведение двойно загрязненного микрокритсаллического фотопровода сульфида кадмия — с Cu и Cl в воздухе при комнатной температуре и вакууме. По данным измерения фотопроводимость уменьшалась с большой инерционностью в сухом и мокром воздухе в исследованном интервале (0,3—1μ) по сравнению с фототоком, появляющимся в вакууме. Это объясняется закономерностью падения соответствующего фототока, полученного у монокристаллов сульфида кадмия. Изменение фототока в рассмотренных случаях оказывалось обратимым.

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EFFECT OF COMPLEX FORMATION ON REACTIVITY[1]

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The different reactions in which reactivity is altered by complex formation are systematized. The manifold relations between the equilibrium and kinetic studies are treated. On the basis of the detailed investigation of several particular reactions general conclusions are made on the mechanism of complex reactions, especially on that of the complex catalysed ones. Several analytical applications are mentioned.

The expression "reactivity" is used quite frequently, but in most of the cases its sense it not exactly defined. We can speak of reactivity in *thermodynamical* and *kinetical* senses. Reactivity means thermodynamically the possibility of a reaction to take place — *i. e.* it is accompanied by a decrease in free enthalpy; kinetically the word indicates the rate of the process, *i. e.* the magnitude of activation energy and of activation entropy.

Complex formation influences reactivity both in kinetical and thermodynamical senses. The effect of complex formation on reactivity in this respect involves several types of reactions and almost innumerable particular reactions. The aim of the present paper is to systematize the corresponding reaction types and to make deductions in general sense from the detailed study of some processes, to establish interdependences and to clarify the manysided connections of equilibrum and kinetical studies.

Systematization of the Processes

It is obvious to differentiate in the systems processes affecting the central ion and the ligands. In case of several reactions, however, the process involves both components of the complex ion: central ion and ligands in the coordination sphere. Concerning the central ion there are only two possible types of reactions where changes in the coordination sphere do not occur. These are:

1,1 Changes in charge of the central ion
1,2 Changes in the quality of the central ion.

Any change in the charge of the central ion is a redox process, the way and possibility of its occurence is the most closely connected with coordination. Thermo-

[1] The paper is a summary of the Theses submitted for the degree „Doctor of Chemical Sciences".

dynamically the complex formation either makes possible or inhibits the reaction with a given reaction partner by shift of the redox potential, and the complex formation is kinetically important since the electron transfer occurs through ligands bound in the coordination sphere. Changes in the quality of the central ion, *i. e.* in case of substitution reactions of the central ion although there are no changes in the coordination sphere, it is obvious that the properties of ligands play an important part in the mechanism of the reaction, and *transiently* there are changes in the coordination sphere of the partners.

From point of view of the reaction of the ligand the following types can be distinguished:

2,1 Substitution reaction of the ligand
2,2 Reactions of the coordinated group(s) of the ligand
2,3 Reactions of parts of the ligand molecule, which do not play a direct part in the coordination

Naturally the reaction of the non-coordinated part of the ligand affect the electron distribution of the donor group bound to the central ion, — frequently to a negligible extent only — thus there is not a sharp boundary between reactions of groups 2,2 and 2,3, the transition is smooth and continuous.

From point of view of both theory and practice, the different catalytic reactions, closely connected with the reactions of the central ion and the ligand, are of extreme importance. Catalytic phenomena of coordination chemistry can be divided into two groups:

3. Catalysis of complex formation reactions
4. Catalytic effect of complexes.

Complex formation reactions catalyzed by complexes are between the two extreme cases. As for the catalysis of complex formation reactions [1] it is purposeful to distinguish the following cases:

3,1 Coordination catalysis
3,2 Induced complex formation
3,3 Electron transfer catalysis
3,4 Heterogeneous catalysis

In case of coordination catalysis the complex formation is preceded by the formation of another transitional complex. Coordination catalysis is connected with the opening of the coordination sphere, what may happen[2] either by means of a ligand or the central ions. Depending on this we distinguish

3,1.1 Ligand catalysis
3,1.2 Metal ion catalysis.

If M central ion reacts only slowly with ligand A and rapidly with ligand D — forming with this latter a thermodinamically less stable somplex — and complex

[2] In course of our recent investigations [2] — after the completion of the dissertation — a new type of coordination catalysis was found: the catalytic effect of the solvent. The $Hg(CN)_2+HgCl_2 = 2HgClCN$ reaction in aqueous medium takes place instantaneously, but in dioxane only very slowly. The rate of the process in dioxane is markedly increased by small amounts of water. This type of reaction can be regarded as a special case of ligand catalysis.

MB reacts also rapidly with ligand A, then ligand D catalyzes the formation of the MA complex. Schematically

$$M + A \overset{k_1}{\rightleftarrows} MA$$

$$M + B \overset{k_2}{\rightleftarrows} MB$$

$$MB + A \overset{k_3}{\rightleftarrows} MBA \overset{k_3'}{\rightleftarrows} MA + B$$

$$k_2, k_3, k_3' > k_1.$$

The catalytic effect of cations appears through the formation of a binuclear transitional complex:

$$MeA_n + B \overset{k_1}{\rightarrow} MeA_{n-1}B + A$$

$$MeA_n + M \overset{k_2}{\rightarrow} A_{n-1}MeAM$$

$$A_{n-1}MeAM + B \overset{k_3}{\rightarrow} MeA_{n-1}B + MA$$

$$MA = M + A$$

$$k_2, k_3 > k_1.$$

In case of induced complex formation the process is accelerated by a simultaneous redox reaction. We can speak of electron transfer catalysis when the following substitution reaction

$$MA + B = MB + A$$

— where ion M is in a higher oxidation state — is accelerated by M ions in lower oxidation state.

Heterogeneous catalysis, having been applied for a longer time in preparation of different complex compounds can be interpreted so that, owing to the adsorption of the complex ion, the coordination sphere is getting loose, *i. e.* the collision of the adsorbed complex with a ligand forming a thermodinamically more stable complex is more effective than a collision in the bulk of the solution.

Classification of complex catalyzed processes can be done according to the type of the catalyzed process.

Kinetical importance of equilibrium studies

The way and extent of a chemical reaction taking place is determined by the quality and quantity of the partners. Thus equilibrium studies are of utmost importance for complex reactions as here we get information about the composition and concentration of ionic species of the given system. Those investigations of equilibria, are of special importance, where the protonation of complexes, formation of polynuclear, mixed and outher-sphere complexes is treated. Namely each chemical reaction requires the interaction of partners, and this may happen just by the reaction types described above.

Protonation of Complexes

Ligands are LEWIS bases, thus, as a rule, competition between the proton and the complex forming metal ion has to be considered. It is reasonable to distinguish complexes of monodentate ligands and chelate complexes. In the protonation of monodentate ligands there are two possibilities: the protonated ligand looses its donor ability, the ligand-metal ion bond breaks, or the protonated ligand is coordinated to the central ion as a dipole. In protonation of hydroxy complexes the corresponding aquocomplexes are formed. Naturally the protonation of polydentate ligands can be various and in its course generally the gradual opening of rings occurs. The kinetical importance of protonation is, that some of the coordination places, occupied by functional groups of the bound ligand they block, become free for interaction with a reaction partner. The method developed by us for determination of stability constants of protonated complexes [3] — in contrast to earlier ones — is applicable even when the protonation takes place at low pH values. The essence of the method is that in case of given central ion and ligand concentrations the extent of decomposition following the increase of hydrogen ion concentration is determined. Corresponding equilibrium constants are obtained by a simple mathematical analysis of the function defined by considering the complex equilibria. The method has been applied for the study of the protonation of Fe(III)-ethylenediaminetetraacetic acid [4] and Fe(III)-1,2-diaminocyclohexanetetraacetic acid [3, 4] complexes.

Formation of mixed complexes

In the coordination sphere of mixed complexes there are at least two different ligands. The number of mixed complexes is very great, especially considering that the coordination sphere of metal ions is saturated even in case of small ligand concentration, partly by the ligand in question and partly by water or other solvent-molecules, resp. The kinetical importance of mixed complexes is obvious, especially for the catalytic effect of the complexes. Namely in these cases besides activator ligand(s) (A) the molecule of the substrate (S) is present also in the coordination sphere of the central ion, that is the formation of an activator-substrate mixed complex (MeA_aS_s) is to be considered. The mole fraction of the mixed complex necessarily changes according to a maximum curve both with changes in concentration of A and S. From this immediately follows that as a rule catalytic activity changes with the concentration of the activator ligand according to a maximum curve. In connection with mixed complexes one of the most important questions is the clearing up of factors influencing the formation and stability of mixed complexes, that is, the connection between stability constants of mixed complexes and "parent complexes" of homogeneous coordination sphere. Partly from data in literature and partly from our own investigations the following two rules can be deduced:

1. If the ratio between stability constants[3] of complexes of a metal ion formed

[3]

$$K_{MY} = \frac{[MY]}{[M]\,[Y]}; \qquad K_{MX} = \frac{[MX]}{[M]\,[X]}$$

$$K_{MYA} = \frac{[MYA]}{[MY]\,[A]}; \qquad K_{MXA} = \frac{[MXA]}{[MX]\,[A]}$$

with different polydenta te ligands (X and Y) is

$$K_{MY} > K_{MX}$$

then the ratio between stability constanst of mixed complexes formed with ligand A is

$$K_{MYA} < K_{MXA}$$

2. The value of equilibrium constant characterizing the stability of $MA_{n/2}B_{n/2}$

$$K = \frac{[MA_{n/2}B_{n/2}]^2}{[MA_n][MB_n]}$$

is greater, the greater the difference between stability constants of the corresponding mother complexes (MA_n and MB_n).

We refer here that the first rule is of general validity, while the validity of the second is markedly influenced by quality of ligands A and B. It was to be valid *e. g.* in case of mercury(II)-cynaide-halide [5] mixed complexes.

In connection with formation of mixed complexes it was pointed out that tetracyano-nickel(II) complex forms with different halide ions pentacoordinated complexes of very slight stability [6]. Nickel(II)-aminopolycarboxilic acid complexes form mixed complexes with cyanide ions [7], and Fe(III)-aminopolycarboxylic acid complexes with hydrogen peroxide [8]. The former rule is valid in respect to their stability, too.

Complexes of outer sphere type

Complexes with saturated coordination sphere may coordinate further ligands in the so called outer coordination sphere. Since changes frequently happen in different redox processes affecting the central ion without even a transient change in the structure of the coordination sphere, it must be supposed that in these cases the electron is conducted by the ligand. From among outer sphere complexes kinetically the most important are those where the ligands bound in the inner sphere contain mobile electrons. Stability constants of such complexes [9] were first time rendered by our experiments, as stability constants of outer sphere complexes of tris (phenantroline)-iron(II) with iodide ions [9] were determined.

Deduction of equilibrium data from kinetical measurements

Rate of chemical reactions is proportional with some powers of the concentration of the partners. Therefore values of velocity — in case of well chosen experimental conditions — may furnish information about the concentration of the particular ionic species, and from this we can calculate equilibrium constants. Kinetical methods formally are similar to spectrophotometric methods, the factor corresponding to the molar extinction coefficient is the rate constant of the particular reaction ways. A marked difference is that in case of optical measurements the concentration is always on the first power what is not always so in kinetical experiments. Constants of the reaction rate change much more sensitively with temperature than extinction coefficients.

Especially in case of catalytic reactions it must be considered that ions present in the system only in small equilibrium concentration and having small thermodynamical stability may markedly influence the experienced rate, since it can be expected that just the intensive factor, the rate constant, will have a great value. In this connection we may refer to investigations described later, in the course of which it became possible to point out the existence of a so far unknown binuclear complex from the kinetical measurements. To determine the stability constants either the increase of activity on the effect of some activator ligands, [10], or in case of a catalytically already active system the decrease of activity on the effect of some inhibitors [11] was measured. From the changes of the rate we make deductions on the concentration of ionic species present in the given system and calculations on the value of stability constants.

Summary of kinetical experiments

Mechanism of redox processes involving the central ion. In this respect the reduction of Cr(VI) was studied. Observing the reduction in presence of ethylenediaminetetraacetic acid [12] it appeared that the cause of the instantaneous complex formation and increase of the rate of reduction is that Cr(VI) forms a complex with EDTA and this complex is reduced more quickly than chromate ion and the reaction results in the formation of an inert Cr(III) EDTA complex. The twofold role of complex formation is very interesting in the reduction of Cr(VI) by Co(II)-aminopolycarbonic acid complexes. The reduction is thermodynamically made possible by complex formation: Cr(VI) oxidizes Co(II) complexes of different aminopolycarboxylic acids but not the Co(II) aquocomplex. But the applied aminopolycarboxylic acids do not contain electrons, thus, if all the coordination places of Co(II) are occupied by functional groups of the ligand, the complex formation prevents the transfer of electron to the oxidizing agent, *i. e.* the coordinated aminopolycarboxylic acid plays the role of an insulator. A condition of the redox process is that water molecule(s) get into the coordination sphere instead of a part of the functional group of the ligand. This is made possible by protonation of the complexes. The necessity of protonation is exhibited by the fact that the rate of reaction, as a function of pH, changes according to a maximum curve. Namely, in case of very low pH values the complexes completely decompose thus the reaction is thermodynamically impossible. At higher pH, where normal non-protonated complexes exist, the mentioned steric inhibitions hinder the interaction of the partners. At intermediate pH values where protonated complexes exist the redox process becomes both thermodynamically and kinetically possible.

The reduction of Cr(VI) takes place in several steps and spectrophotometric investigation unequivocally prove the existence of at least one intermediate. In case of reduction of Cr(VI) by Co(II) EDTA complex [13] the intermediate is relatively stable and its study and the reaction kinetical data show that it is a heteronuclear complex containing Co(III) and Cr(IV) central ions.

Reaction of the ligand. Our investigations aimed to make suppositions on the structure of the complex from changes in the reactivity of the ligand. In acidified medium free EDTA is rapidly oxidized by permanganate and — under favourable conditions — the reaction can be applied to determine EDTA permanganometri-

cally, too [14]. In the course of these experiments it has been also pointed out that in presence of Bi(III) of equivalent or excess amount, EDTA is not oxidized, that is complex formation defends the ligand against the oxidizing effect of permanganate. This phenomenon can be usefully applied in different analytical methods, and at the same time it suggests that in the Bi(III) EDTA complex all the function groups are coordinated to the central ions, *i. e.* there is no protonation even at relatively great acidity. For sake of comparison experiments were done with the oxidation of Cr(III) EDTA complex by permanganate [15]. As it is known, this complex is substitution inert, so free EDTA does not get into the solution during the experiment, and as it is proved by a lot of experiments, EDTA occupies in this complex only 5 coordination places. Therefore it can be expected that now the oxidation of the ligand will be more rapid. This expectation had been proved by our experiments, where the decrease in the permanganate concentration was followed by measuring the light absorption. It was also observed that the rate changes with the pH according to a maximum curve. This hardly can be interpreted otherwise than with the existence of Cr(III) EDTA in acidified medium in two forms having different reactivity, and of these the non-protonated ionic species oxidizes more rapidly.

Catalytic decomposition of hydrogen peroxide is the most thoroughly studied process of the reactions catalyzed by complexes. Fe(III)-triethylenetetramine complex is the most effective catalyst of the decomposition of hydrogen peroxide. It has been pointed out [16] that parallel to the catalytic decomposition of hydrogen peroxide, the oxidation of triethylenetetramine by hydrogen peroxide, being present in great excess to Fe(III), also takes place, and this process is also catalyzed by the triethylenetetramine-Fe(III) complex. The rate-decrease in time of the catalytic reaction can also be ascribed to this process. On the basis of our experiments the great catalytic activity of triethylenetetramine-Fe(III) complex is the result of the following factors:

1. The stability of the complex is much greater than that of ethylenediamine-Fe(III) or diethylenetriamine-Fe(III) complexes, and makes possible to reach relatively great complex concentration even about pH = 10.

2. The direct source of catalytic activity is the common effect exerted on bound hydrogen peroxide of the central ion and hydroxide ion ligand bound at the fifth coordination place. So the catalytic ineffectivity of tetraethylenepentamine-Fe(III) complex, although it is more stable than triethylenetetramine-Fe(III), can be interpreted.

3. In the formation of catalytic activity a decisive factor is that the electrically neutral ligand does not screen considerably the positive charge of the central ion, thus its electron withdrawing effect is greater what results in weakening of the O—O bond.

Our investigations supported the experience that the common Fe(III) aminopolycarboxylic acid complexes are catalytically ineffective for the decomposition of hydrogen peroxide. It was also observed [17] that in acidified medium the rate of decomposition of hydrogen peroxide catalyzed by Fe(III) changes with the concentration of EDTA according to a maximum curve, *i. e.* it must be considered by all means that in this system, owing to the Fe(III) EDTA interactions besides the inactive normal complex another with great catalytic activity is formed. This is probably a binuclear complex, in which the source of the increase of activity is the concerted effect of the two central ions on the same substrate molecule.

Catalytic effect of oxygen carrying complexes. It has been established, that the autoxidation of ascorbic acid is catalyzed both by Co(II)-glycylglycine [18] and Co(II)-histidine complexes [19], but the mechanism of the process is different in the two cases. In case of Co(II)-glycylglycine complex the formation of the oxygen-carrying complex is catalyzed by ascorbic acid, and decreases the rate of irreversible oxidation leading to Co(III). In case of Co(II)-histidine complex, however, the rate of irreversible oxidation increases in presence of ascorbic acid. Further difference, that while in case of Co(II)-glycyglycine the catalytic activity completely ceases following the irreversible oxidation, there is only a decrease in activity at the Co(II)-histidine complex.

Activation of molecular hydrogen. From earlier investigations it is known that reduction processes with molecular hydrogen are catalyzed by some metal ions and complexes, resp. Starting from theoretical considerations, the effect of fluoride ions on the reaction of silver(I)-ion with molecular hydrogen was studied [9]. The rate of the process can be described by the following equation:

$$\frac{d(H_2)}{dt} = \frac{1}{2}\frac{d(Ag^+)}{dt} = \frac{kC_{Ag}C_F(H_2)}{1+k'C_F}.$$

The empirical rate equation can be interpreted so that the reduction of the less stable monofluoro-silver(I) complex takes place at about ten thousand times more rapidly than that of the silver(I) aquocomplex. The experiments rendered possible the determination of both the rate constant and the stability constant of the complex. The great activation effect of fluoride ion undoubtedly is the result of the concerted effect of central silver(I) ion and coordinated fluoride ion. Considering the steric conditions it must be supposed that the polarizing effect of fluoride ion appears by means of a water molecule through a hydrogen bridge bond.

As to catalyzed complex formation reactions we have found the first instance of specific ligand catalysis and of induced complex formation. Namely, it has been pointed out, that the formation of thiocyanato-Cr(III)-complexes is catalyzed by carbonate ion [1], and — as it had already been pointed out in connection with the catalytic effect of oxygen-carrying complexes — that the autoxidation of ascorbic acid accelerates the formation of oxygen carrying Co(II)-glycylglycine complex [18]. In connection with catalysis of the aquotization processes by metal ions we gave a direct experimental proof that this catalytic effect appears through the transient formation of a binuclear complex [20]. In the course of aquation of hexacyano-Fe(II) complex, catalyzed by mercury(II), it was cleared up which ionic species are catalytically effective, and it was established that the effect of different cations and anions can be interpreted by complex and ionic pair formation, respectively [21].

Analytical Applications

The effect of complex formation on the reaction rate is the basis of several analytical methods. The fact, that on the effect of excess of cyanide ion Ni(II) EDTA transforms to tetracyano-Ni(II) complex instantaneously while Ni(II) DCTA only slowly, makes possible the simple spectrophotometric determination of DCTA in presence of great amounts of EDTA [8].

On the basis of the inhibiting effect of complex formation on the oxidation of ligands, the permanganometric determination of chromium(III) [22], bismuth(III)

and iron(III) has been elaborated, and it was found, that permanganometric determinations can be carried out in presence of EDTA, if EDTA is transformed into complex by bismuth(III) [14].

The extreme effectivity of the triethylenetetramine Fe(III) complex on the decomposition of hydrogen peroxide made possible the elaboration of a simple permanganometric method [23] for the determination of ultramicro amount of iron (0,03—1,2μg).

* * *

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ВЛИЯНИЕ ОФОРМЛЕНИЯ КОМПЛЕКСОВ НА РЕАКЦИОННУЮ СПОСОБНОСТЬ

М. Т. Бек

Автором дается классификация типов реакций, где оформление комплексов ведет к изменению реакционной способности. Далее он трактует многосторонную связь равновесных и кинетических экспериментов, и исходя из тщательного изучения некоторых процессов, даются общие сведения о механизме комплексных реакций, особенно о механизме реакций катализованных комплексом. Автор также указывает на несколькие аналитические применения.

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SYNTHESIS OF SUBSTANCES EFFECTING C. N. S. V

Synthesis of Some New Tertiary Amino-p-Alkyl-Aryl-Propene and -Propane Derivatives

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As a continuation of earlier synthetic investigations, several p-alkyl acetophenones were prepared by means of the FRIEDEL—CRAFTS reaction, which were converted into substituted N-piperidino-aralkylpropanones with the help of the MANNICH condensation. The aforesaid ketones were reduced to alcohols and dehydrated with perchloric acid to propenes. After repeated catalytic reduction propane-derivatives were obtained.

ISSEKUTZ, PÓRSZÁSZ and NÁDOR [1] were the first of deal comprehensively with the synthesis and pharmacological activities of arylketones [2, 3]. A considerable number of aminoketones belonging to this group had been known since MANNICH's [4] investigations, however, it was shown that not alone aminoketones exert CNS effects but other groups of MANNICH bases, too [7].

The authors had earlier devised a method to produce N-tertiary-amino-aralkyl-ketones [5] this method, however, proved to be too *involved* and complicated [6], consequently we continued to find an other way concerning the synthesis of amino-propane. Simultaneously, efforts were made to separate the stereoisomers (cis and trans) of amino propenes. The necessary aminoketones for the synthesis of

$$R.C_6H_4.CH=CH.CH_2-N.R_1R_2$$

have been made using MANNICH's condensation.

In the above mentioned general formula R is alkyl and $N.R_1R_2=N(C_2H_5)_2$ (diethylamino), $N.C_5H_{10}$ (piperidino), $N.C_4H_8$ (pyrrolidino) and $N.C_4H_8O$ (morpholino) radicals.

The aralkyl-compounds were synthetized with help of FRIEDEL—CRAFTS-reactions (8), using dry $AlCl_3$ as catalyst. As by-products di-, tri-, etc. alkyl-benzenes (I.) [9] were always obtained.

The same condensation was also used for the synthesis of p-aralkyl-acetophenones (II):

I.,

$$R.CH_2Cl + C_6H_6 \xrightarrow{AlCl_3} R.CH_2.C_6H_5 + HCl$$

II.,

$$R.CH_2.C_6H_5 + CH_3.\overset{\overset{O}{\|}}{C}.Cl \longrightarrow R.CH_2.C_6H_4.\overset{\overset{O}{\|}}{C}.CH_3 + HCl$$

R means here hydrogen or shorter p-alkyl groups.

The FRIEDEL—CRAFTS reactions were in general carried out in CS_2 or nitrobenzene solvents, sometimes, however, the excess of alkyl-benzene served as solvent.

The p-aralkylacetophenones were converted into aminoketones (MANNICH condensation). These reactions were catalysed by the presence of hydrochloric acid.

The rate of the MANNICH condensation depends on the reactivity of the hydrogen atoms of the methyl groups, whereas the reaction with p-nitro-acetophenone takes place momentarily, p-chloro-and p-hydroxy-acetophenones react very slowly and give a poor yield.

The first step of the MANNICH condensation of this type may proved into two directions, depending on reaction conditions, as to whether formaldehyde reacts first with the mobile methylene group (a) or with the amino group (b).

III.,

$$\begin{array}{lll} & R.\overset{\overset{O}{\|}}{C}.CH_3 + CH_2O & R_1R_2.NH + CH_2O \\ a) & \downarrow & b) \quad \downarrow \\ & R.\overset{\overset{O}{\|}}{C}.CH_2.CH_2OH & R_1.R_2N.CH_2OH \end{array}$$

$$\xrightarrow{-H_2O} RC.CH_2.CH_2.N.R_1.R_2 \quad (\overset{\overset{O}{\|}}{C})$$

R and N R_1R_2 mean the same as above.

The described reactions, however, indicate merely, the main direction of the reaction, however, on the basis of our experiments other side reactions are minimal.

When the acetophenone components are not sufficiently reactive and, as a consequence, the condensation would require a long time, the side reaction may

reappeare and the formation of a di-/-N-dialkyl/-methane can be expected:

$$R_2.R_1.N.CH_2.OH + NH.R_1.R_2$$
$$\downarrow$$
$$R_2.R_1.N.CH_2.N.R_1.R_2$$

In fact, we were able to isolate dipiperidino-methane-dihydrochloride (mp.: 246 °C), it could be separated from the main reaction product only by fractionate crystallization.

The reactivity of the p-aralkyl-acetophenone, synthetized by us, was only average consequently, the condensation required in general from 4—7 hours. The yield of the condensation, calculated for p-aralkly-acetophenone, ranged between 50—60%. We tried to apply FRY's [10] method in order to reduce the reaction time in several cases, however, without any result. Mostly, the above mentioned reaction path with piperidino hydrochloride failed, as piperidine-hidrochloride did not dissolve in the mixture of benzene-nitrobenzene, and heterogeneous conditions do not favor this type of condensation.

The next step was the reduction of the aminoketones. Initial experiments, carried out with Zn/Hg, were unsuccessful. A catalytic method, described by FODOR and KOVÁCS (12), proved to be the best. These authors obtained tyramine, respectively methyl-tyramine, from the ketone using the above method.

The reduction was made in acetic acid in the presence of perchloric acid with a Pd/(charcoal) catalyst. This reduction resultated in the expected alcohol but only at room temperature. The Pd/C-reduction was modified, according to the solubility of the substances, using dilute acetic acid, alcohol and, in many cases, water. Thus, the expected alcohol was obtained in quantitative yield.

The reduction proceeds as follows:

IV.,
$$R.\overset{\overset{O}{\|}}{C}.CH_2.CH_2.N.R_1R_2$$
$$\downarrow$$
$$R.CHOH.CH_2.CH_2.N.R_1.R_2$$

The formed racemic aminopropanol was and extracted with ether. A separation into the optically active alcohols has not been attempted.

The reduction was followed by dehydration for the sake of the formation of the unsaturated products:

V.,
$$R.CH.OH.CH_2.CH_2.N.R_1.R_2$$
$$\downarrow -H_2O$$
$$R.CH=CH.CH_2.N.R_1.R_2$$

Pyrolytic dehydration appeared too drastic in our case consequently milder dehydration conditions were applied [17, 18] and, finally perchloric acid-dehydration proved to be the most adequate [12]. At any rate, certain modifications had to be made.

To ensure the cis-isomers one has to start from the pure base because the presence of chloride ion traces favors according to our experiences the formation of trans-isomers.

Thus dehydration was carried out in methanol or benzene solution. The unsaturated compound was isolated as free bases.

The cis-isomer is very sensitive, leached with NaOH, it is transformed into 2-aminopropanol, hence neutralize the solution, $NaHCO_3$ was used. The cis-isomer is also sensitive to temperature and turns into the trans-isomer due to the chloride ion.

Having obtained propene-derivatives following dehydration in the presence of a Pd/C-catalyst, and upon hydrogenation at atmospheric pressure in acetic acid, we obtained the saturated propane derivatives.

VI. $R.CH=CH.CH_2.N.R_1.R_2$

$R.CH_2.CH_2.CH_2.N.R_1.R_2$

The thus synthetized compounds were pharmacologically active. Above all, they influence the CNS, they also show intensive antinicotinic activity, inhibit the counter extensor reflex, some of them produce prolonged muscle relaxation, very frequently, they prevent the spasms produced by electroshock.

Experimental

The m. p. are determinated by „Boëtius" apparatus and corrected.

3-piperidino-propiophenone HCl (I).

12,1 g of piperidine HCl, 12 g of acetophenone 1,5 g of 73% paraformaldehyde and 0,25 ml. of cc. HCl are dissolved, suspended in 50 ml of absolute ethanol and refluxed for 1,5 hour, 1,5 g of 73% paraformaldehyde is added and refluxed again for 1.5 hour. It is filtered hot and kept in an icebox for a few hours. A crystalline substance appears, which is then filtered and dried. The substance is recrystallized from a mixture (1:6) of alcohol-acetone. M. p.: 190—191 °C.
(Analytical data concerning the substances to be described and the substance I. are in Table I.)

1-phenyl-piperidino-propanol-1 (II).

20 g of I is solved in 100 ml of water and in 5 ml of acetic acid, 4 g of Pd/C catalyst is added and it is hydrogenated at atmospheric pressure as soon as the calculated amount of hydrogen is used up, the reaction is stopped and the catalyst filtered. The solution is rendered alkaline with 2 N NaOH and extracted with ether. The etheric solution is collected and dried on anhydrous Na_2SO_4 it is filtered and the ether distilled: there remains a pale yellow oil, which is distilled under completely anhydrous conditions a crystalline substance results. M. p.: 54—55 °C.
The hydrochloride of the mentioned substance was prepared (II) its. M. p. is = 151 °C.

1-phenyl-piperidino-propene 1-HCl (trans) III.

3 g of II-hydrochloride is dissolved in the mixture of 1 ml of $HClO_4$ in 15 ml of acetic acid and kept at 150 °C for 45 minutes: upon cooling, it is diluted with water and rendered slightly alkaline, it (pH 8) with NaOH. The base thus obtained in extracted with ether, and the ether solution evaporated. The remaining brownish solution is thrice dissolved in abs. ethanol and distilled to remove the water. The

weight of the thus obtained base is 2 g. It is dissolved, in an alcohol-acetone mixture (1:6) and a hydrochloride is separated with an absolute ether hydrochloric acid mixture. (2 g of hydrochloride). The latter is suspended in hot acetone and alcohol is added to it as long as it is not dissolved. Upon cooling white needles appear. M. p.: 213 °C.

1-phenyl-3 piperidino-propene-1-HCl (cis) (IV).

3 g of base II is dissolved in 30 ml of abs. methanol and cooled in a salt-ice mixture. While constantly shaking it, 5 ml of cc. H_2SO_4 is dropwise added to the cooled solution. Then it is refluxed with 0,2 g of $CuSO_4$ for three hours. The boiling solution rendered alkaline with $NaHCO_3$ a little water is added, and the base extracted with ether. The ether solution is dried (anhydrous $MgSO_4$), filtered and the ether is evaporated *in vacuo*, the residue is dissolved in absolute ethanol and the solution in concentrated. The weight of the base is 1,8 g, it is dissolved in ether and a hydrochloride is prepared with the calculated amount of hydrochloric acid, it immediately precipitates (M. p.: 155—156 °C). The amorphous substance thus obtained is purified by recrystallization. M. p.: 174—176 °C.

p-methylacetophenone (V) (19).

A three-necked flask is supplied with a condenser and the top of it with a hydrochloric acid trap, stirrer and a dropping funnel, it is placed in an ice bath. 103,6 g of abs. toluene are poured in and 94,3 g of purified $AlCl_3$ is suspended in the solution while stirring, 29,4 g of glacial acetic acid is added within 30 minutes. Following dosaging it is kept in a water bath for an other hour, then the reaction mixture is poured in a mixture of 300 g of ice and 25 ml of cc. HCl. The organic phase is separated and washed with 50 ml of water, then dried (anhydrous $CaCl_2$). The residue of tolune is destilled and the substance is then fractionated in vacuo. The weight of the obtained material is 46,9 g. B. p.: 182 °C.

1-p-methyl-phenyl-3 dipiperidino-propanone-1-HCl (VI).

13,4 g of V is condensed as described with compound I. The weight of the crude product is 14 g, M. p. 180—181 °C. It is recrystallized from a mixture of alcohol and acetone. Yield: 10 g. B. p.: 182 °C.

1-p-methyl-phenyl-3-piperidino-propanol-1 (VII).

11 g of VI was prepared by a Pd/C reduction as described with compound II. The weight of the obtained base is 7,4 g. M. p. of the base: 79—81 °C. M. p. of hydrochloride: 148 °C.

1-p-methyl-phenyl-3-piperidino-propene-1 (trans) (VIII).

3 g of VII (hydrochloride) was made by using method III. 1,9 g of substance was obtained at m. p.: 237 °C. It was recrystallized from a hot acetone-alcohol mixture. With needles were separated. M. p.: 249 °C.

Using the method applied to the synthesis of IV it was attempted to prepare the cis-isomer, but here and in other cases the attempts failed. In every cases the trans-isomers were formed. The trans-isomer is the more stabile modification. Consequently, we shall not deal with this method any longer and describe merely the preparation of the trans-isomer.

Table I

Names of substances	Number of substances	M. w.	Summary forms
3-piperidino-propiophenone-HCl	I.	253,76	$C_{14}H_{20}NOCl$
1-phenyl-3-piperidino-propanol-1	II.	255,77	$C_{14}H_{22}NOCl$
1-phenyl-3-piperidino-propene-1-HCl (trans)	III.	237,76	$C_{14}H_{20}NCl$
1-phenyl-3-piperidino-propene-1-HCl (cis)	IV.	237,76	$C_{14}H_{20}NCl$
1-(p-methyl-)-phenyl-3-piperidino-propanone-1-HCl	VI.	267,79	$C_{15}H_{22}NOCl$
1-(p-methyl-)-phenyl-3-piperidino-propanol-1	VII.	269,8	$C_{15}H_{24}NOCl$
1-(-p-methyl-)-phenyl-3-piperidino-propene-1 (trans)	VIII.	251,78	$C_{15}H_{22}NCl$
1-(-p-ethyl)-phenyl-3-piperidino-propanone-1-HCl	X.	281	$C_{16}H_{24}NOCl$
1-(-p-ethyl)-phenyl-3-piperidino-propanol-1	XI.	223,34	$C_{14}H_{25}NO$
1-(-p-ethyl-)-phenyl-3-piperidino-propene-1 (trans)	XII.	205,33	$C_{14}H_{23}N$
1-(-p-i-propyl-)-phenyl-3-piperidino-propanone-1-HCl	XVII.	295,84	$C_{17}H_{26}NOCl$
1-(-p-i-propyl-)-phenyl-3-piperidino-propanol-1-HCl	XVIII.	261,34	$C_{17}H_{27}NO$
1-(-p-i-propyl)-phenyl-3-piperidino--propene-1-HCl (trans)	XIX.	245,37	$C_{17}H_{25}N$
1-(-p-t-butyl-)-phenyl-3-piperidino-propanol-1-HCl	XXIII.	309,87	$C_{18}H_{28}NOCl$
1-(-p-t-butyl-)-phenyl-3-piperidino-propanol-1-HCl	XXIV.	276,42	$C_{18}H_{30}NO$

Physical data (mp., bp.,, n_D^{20})	Calculated				Found				Yield %
	C%	H%	N%	Hlg%	C%	H%	N%	Hlg%	
190 – 191°C	66,4	7,97	5,53	14,17	66,29	7,87	5,41	14,30	63
54 – 55°C	65,67	8,60	5,49	13,72	65,75	8,65	5,69	13,85	81
213°C	70,88	8,43	5,9	15,12	70,67	8,65	5,75	15,20	68
174 – 176°C	70,88	8,43	5,88	15,12	70,76	8,35	5,90	15,35	62
182°C	67,21	8,36	5,24	13,1	67,30	8,40	5,20	13,05	37
148°C	66,91	8,92	5,18	13,01	66,95	8,88	5,30	12,93	85
249°C	75,47	10,37	5,55	7,58	75,32	9,92	5,60	7,62	38
183 – 184°C	68,32	8,54	4,98	12,45	68,40	8,56	4,79	12,30	52
140°C	67,84	9,18	6,26	–	67,92	9,21	6,40	–	54,4
240°C	81,81	11,21	5,28	13,20	81,75	11,20	5,22	13,15	96
178 – 180°C	69,01	8,85	4,73	11,98	68,93	9,0	4,68	11,73	72,5
186°C	68,54	9,47	4,70	11,91	78,05	10,29	4,90	12,10	50
237°C	72,95	9,53	5,95	12,6	73,02	9,42	6,05	12,7	74,2
164 – 165°C	67,82	9,68	4,51	12,11	67,91	9,45	4,60	12,07	54,2
196°C	69,45	9,64	5,06	11,25	69,31	9,72	5,15	11,34	80,7

Table I (contd.)

Names of substances	Number of substances	M. w.	Summary forms
1-(-p-t-butyl)-phenyl-3-piperidino-propanone-1 (trans)	XXV.	258,41	$C_{18}H_{28}N$
1-piperidino-3-(-p-cyclohexyl-phenyl-)-propanone--3-HCl	XXVII.	335,83	$C_{20}H_{30}NOCl$
1-piperidino-3-(-p-cyclohexyl-phenyl-)-propanol--3-HCl	XXVIII.	337,85	$C_{20}H_{32}NOCl$
1-piperidino-3-(-p-cyclohexyl-phenyl-)-propene-3-HCl	XXIX.	319,83	$C_{20}H_{30}NCl$
1-piperidino-3-(-p-cyclohexylphenyl-)-propene-HCl	XXX.	321,85	$C_{20}H_{32}NCl$
1-piperidino-3-(-p-methyl-phenyl-)-2-methylpropanol--3-HCl	XXXI.	283,75	$C_{16}H_{26}NOCl$
1-piperidino-3-(-p-methylphenyl-)-2-methyl-propene--3-HCl	XXXII.	266,75	$C_{16}H_{25}NCl$
1-piperidino-3-(-2-naphtyl-tetrahydro-5, 6, 7, 8-)--propenon-3-HCl	XXXIII.	307,65	$C_{18}H_{26}NOCl$
1-piperidino-3-(-2-naphtyl-tetrahydro-5, 6, 7, 8-)--propanol-3-HCl	XXXIV.	309,67	$C_{18}H_{28}NOCl$
1-piperidino-3-(-2-naphtyl-tetrahydro-5, 6, 7, 8-)--propene-3-HCl	XXXV.	291,65	$C_{18}H_{26}NCl$
1-(-β-oxyethylaminomethyl-)-3-phenyl-propene-3-HCl	XXXVI.	227,58	$C_{12}H_{18}NOCl$
1-(-β-chloromethylamino-methyl-)-3-phenyl-propene--3-HCl	XXXVII.	246,03	$C_{12}H_{17}NCl_2$
1-(-β-piperidino-ethylamino-methyl-)-3--phenylpropene-3-2-HCl	XXXVIII.	311,12	$C_{17}H_{28}N_2Cl_2$
1-(-p-i-propyl-)-phenyl-3-piperidino-propane-HCl	XXXIX.	281,86	$C_{17}H_{27}NCl$

Physical data (mp., bp., n_D^{20})	Calculated				Found				Yield %
	C%	H%	N%	Hlg%	C%	H%	N%	Hlg%	
220°C	73,72	9,55	5,41	11,94	73,65	9,40	5,60	11,80	87,9
188°C	71,52	8,96	4,18	10,71	71,60	8,99	4,23	11,10	69
217°C	71,32	9,56	4,14	10,50	71,54	9,81	4,30	10,78	56
234 – 235°C	74,50	8,92	4,36	12,12	74,56	9,22	4,50	12,19	70,5
199 – 200°C	74,75	9,95	4,34	11,02	74,53	9,58	4,45	11,38	60,5
130 – 131°C	67,40	9,12	4,93	12,42	67,40	9,13	4,90	12,49	51,6
200°C	72,01	9,47	5,23	13,28	72,00	8,98	5,35	13,43	42,7
178,5°C	68,80	8,47	4,55	12,42	68,94	8,32	4,70	12,24	85
160°C	65,02	9,13	4,52	11,32	64,92	9,00	4,65	11,25	73
224 – 225°C	74,50	8,95	4,80	12,12	74,56	9,15	5,00	12,19	64
121°C	63,45	7,49	6,15	15,61	63,24	8,07	6,25	15,47	68,3
147°C	58,76	6,95	5,69	28,90	58,35	7,24	5,75	29,00	70,5
248 – 250°C	65,52	9,08	4,51	22,68	65,34	9,24	4,65	22,43	47,6
203 – 204°C	72,43	10,02	4,97	12,58	72,40	10,12	5,05	12,72	98

p-ethyl-acetophenone (IX) (20).

A mixture of 12 g of ethylbenzene, 15 g of acetyl-chloride and 50 ml of petroleum ether is placed in a three-necked flask supplied with a refluxing condenser and stirrer, in one of the necks a dry stoppered test tube is fixed. It is strongly cooled and 15 g of $AlCl_3$ is added in small doses, at constant stirring, for about half an hour. It is refluxed on the water bath for some time and the complex is poured into ice water and treated in the usual way. Yield: 9,53 g. B. p.: 132—136 °C/40 mm. $n_D = 1{,}5275$.

1-(-p-ethyl-)-phenyl-piperidino-propanone-1-HCl (X).

14,8 g of IX is condensed according to method I. Yield: 14,62 g. M. p.: 183—184 °C.

1-(-p-ethyl-)-phenyl-3-piperidino-propanol-1-HCl (XI).

8,62 g of the hydrochloride of X is reduced and thus 7,95 g of base is obtained. M. p. of the hydrochloride: 140 °C.

1-(-p-ethyl-)-phenyl-3-piperidino-propene-1-HCl (trans) (XII).

3 g of XI was dehydrated using method III. Yield: 2,27 g base. M. p. of the hydrochloride: 240 °C.

n-propyl bromide (XIII) (21).

A mixture of 500 g of 48% HBr, 150 g of cc. H_2SO_4 and 144 g of n-propanol is warmed on a water bath and 120 g of cc. H_2SO_4 is slowly added dropwise. The simultaneously, propyl bromide is distilled. The cooler and the receiver are cooled with ice water. The substance formed is washed with the equivalent of cc. HCl, water, 5% $NaHCO_3$ and then again with water. It is dried (anhydrous $CaCl_2$), filtered and distilled. Yield: 134 g. B. p.: 70—73 °C. Product: 45% $n_D = 1{,}4321$.

Isopropyl chloride (XIV).

1,5 l of cc. HCl (36%) is placed in a 2,5 l round-bottomed flask provided with a cooler and with a dropping funnel and heated to 60 °C. 500 ml of isopropanol is added dropwise. It is kept in a hot water bath for 8—10 hours. The isopropyl chloride formed is distilled under ice cooling. Yield: 180 g. B. p. 34,5 °C. Product: 35,3%.

Isopropyl benzene (XV) (21).

A two liter, three-necked flask, provided with stirrer, cooler and with a dropping funnel, is placed in a salt-ice bath. An acid trap is fixed to the end of the cooler. 16 g of $AlCl_3$ is suspended in 611 ml of benzene in the flask and the mixture of 262 ml of benzene and 120 g of n-propyl bromide or of isopropyl chloride is added to it. The mixture is heated to 80 °C for two hours.

The upper phase is then removed, washed with diluted NaOH, and with water, and dried (anhydrous $MgSO_4$). Yield: 114,75 g. B. p.: 82—85 °C/43 mm. Product: 96% $n_D = 1{,}4975$.

The isopropyl compound (XV) may be prepared, using another method, namely a modification of that published by MAZONSKI and his coworker (22).

675,5 g of dried benzene and 266 g of $AlCl_3$ are poured in a round-bottomed flask, provided with a 2-liter stirrer, reflux condenser and a thermometer. The reaction

mixture is cooled to 0 °C (with a salt-ice mixture, containing very little salt.) 120.2 g of isopropyl alcohol is added dropwise to it, stirring very intensively for about an hour. The inner temperature during the reaction must be constantly kept between 0° and 5 °C. Following the addition of isopropyl alcohol, the stirring is continued for about 2 hours until elimination of the hydrochloric acid, raising the temperature to 18—20 °C. Then the solution is poured over the mixture of 200 ml of cc. HCl and 600 g of ice. The benzene phase is gradually separated, dried (anhydrous $CaCl_2$), filtered, and the excess of benzene driven off the isopropyl benzene is the distilled at atmospheric pressure. B. p.: 151—153 °C. Yield: 116 g $n_D = 1{,}4935$.

p-isopropyl-acetophenone (XVI) (23).

135 g of $AlCl_3$ is solved in 135 ml of CS_2 and cooled to −5 °C. The mixture of isopropyl benzene and 87,02 g of acetyl chloride, under cooling and constant stirring, is dropped into the system at such a rate as not to allow the temperature to rise over +5 °C. The solution is heated to 15 °C, and it is poured into a mixture of 143 ml of cc. HCl and 600 g of ice. The organic phase is separated and the aqueous part is extracted 3 times with 150 ml of ether. The phase formerly separated and the etheric phase are combined and dried (anhydrous K_2CO_3). Yield: 115 g. B. p.: 155—158 °C/42 mm. B. p.: 122—124 °C/10 mm $n_D = 1{,}5193$.

1-(-p-i-propyl-)-phenyl-3-piperidino-propenone-1-HCl (XVII).

18,2 g of XVI is condensed into XVII using method. I. Yield: 21,34 g. M. p.: 176—178 °C.

i-(-p-i-propyl-)-phenyl-3-piperidino-propanol-1-HCl (XVIII).

29,5 g of XVII is reduced by method II. Yield: 14,75 g base. M. p. of the hydrochloride: 155 °C.

i-(-p-i-propyl-)-phenyl-3-piperidino-propene-1-HCl (trans) (XIX).

3 g of the hydrochloride of XVIII are dehydrated by method III. Yield: 2,1 g hydrochloride. M. p.: 237 °C.

Preparation of t-butylchloride (XX) (21).

25 g of absolute t-butanol and 85 ml of cc. HCl are placed in a 250 ml separatory funnel and constantly shaken for 20 minutes. The two phases are separated. The t-butylchloride formed is washed with 20 ml of 5% $NaHCO_3$ and with water, dried (anhydrous $CaCl_2$) and distilled. Yield: 16 g. B. p.: 49—52 °C. $n_D = 1{,}3859$

t-butylbenzene (XXI) (24).

In a well cooled mixture of 150 g of benzene and 50 g of $AlCl_3$, 44 g of t-butylchloride is slowly dropped in for 48 hours. It is stirred at room temperature for two hours and poured into ice water and washed with distilled water, then warmed on a water bath with dilute NaOH for half an hour. The two phases are separated. It is washed with water, and dried (anhydrous $NaSO_4$), filtered, and distilled. Yield: 20 g of t-butylbenzene $n_D = 1{,}502$. The yield of the product, treated with abs. benzene, and the mixture well cooled, may be increased to 50%.

p-t-butyl-acetophenone (XXII) (25).

81 g of $AlCl_3$ is solved in 81 ml of SC_2 and cooled to −5 °C. A mixture of 80 g of t-butylbenzene and 51,6 g of acetyl chloride is dropwise added to at constant cooling and stirring in such a way as not to allow the temperature to rise above −5 °C. Then the mixture is heated to 15 °C, thereafter poured into a mixture of 400 g of ice and 100 ml of cc. HCl. The solution is extracted with 4 ×200 ml of ether. The combined etheric extracts are dried (anhydrous K_2CO_3), the solvent is evaporated and the residue is distilled. Yield: 50,5 g. B. p.: 134—135/11 mm. $n_D^{20} = 1{,}5179$.

1-(-p-t butyl-)-phenyl-3-piperidino-propanone-1-HCl (XXIII).

39,2 g of XXII is continued, using method I. Yield: 33,4 g. M. p.: 164—165 °C.

1-(-p-t butyl-)-phenyl-3-piperidino-propanol-1-HCl (XXIV).

33,4 g of XXIII compound is reduced to the alcohol by method II. Yield: 24,9 base. M. p. of the hydrochloride: 196 °C.

1-(p-t-butyl-)-phenyl-3-piperidino-propane-1-HCl (trans) (XXV).

Water is eliminated with $HClO_3$ from 3 g of XXIV hydrochloride. Yield: 2,18 g base. M. p. of hydrochloride: 220 °C.

p-cyclohexylacetophenone (XXVI) was obtained by the method, described by LUTZ *et al.* (26).

1-piperidino-3-p cyclohexylacetophenyl-propanone-3-HCl (XXVII).

20 g of piperidino NCl, 32 g of XXVI, 9 g of paraformaldehyde is refluxed in 80 ml of absolute ethanol for two hours, thereafter 9 g of more paraformaldehyde is added to the mixture and it is continued to reflux for 3 hours. It is filtered warm, the solution is evaporated to half and 50 ml of acetone is added to it the amino-ketone is crystallized, filtered, washed with acetone. M. p.: 183—184 °C. Yield: 37 g. Crystallized from acetone-ethanol, M. p.: 188 °C.

1-piperidino-3-(-p ciclohexylphenyl-)propanol-3-HCl (XXVIII).

8 g of XXVII is hydrogenated at room temperature in 20 ml of a methanol solution in the presence of 0,1 g of Pt-oxide catalyst, (at atmospheric pressure). To take up the calculated amount of hydrogen about four hours are needed. After filtering when turbidity commences, absolute ether is added and it is kept standing for some hours in refrigerator 4,5 g of substance crystallizes. M. p.: 212 °C. Recrystallized from an acetone-methanol mixture the m. p. is 217 °C.

1-piperidino-3-(p-cyclohexylphenyl-)propene-3-HCl (XXIX).

1,5 g of XXVIII is dissolved in 10 ml of acetic acid and, it is refluxed in the presence of 0,4 ml of 9,4 N $HClO_3$ for 50 minutes. Upon cooling, the perchlorate of the unsturated compound in precipitated in lamellated crystals, it is filtered and dried. (M. p. 166 °C). It is dissolved in 10 ml of acetone and rendered alkaline with aqueous sodium carbonate. The base is crystallized from the solution, it is filtered and washed with water. M. p.: 67—68 °C (1 g). It is dissolved in ethanol and the hydrochloride prepared with ethanol hydrochloric acid. M. p. 232°C. Recrystallized from ethanol-acetone. M. p.: 234—235 °C.

1-piperidino-3-(p-cyclohexylphenyl)propane-HCl (XXX).

5 g of XXIX is hydrogenated in 30 ml of acetic acid in the presence of 1,6 g of Pd/C, at room temperature and at atmospheric pressure. The calculated amount of hydrogen is taken up in about 5 hours, if not, 1,3 ml of 9,8 N $HClO_3$ is added to the solution and the hydrogenation is continued at 85 °C for further 5 hours. After cooling, it is filtered, potassium acetate is added to the filtrate to remove the perchlorate residue. It is filtered again and the solvent is distilled in vacuo. The oily residue is dissolved in 20 ml of water and rendered alkaline by 10% NaOH it is extracted with ether. The ether extract is washed with water and dried (anhydrous Na_2SO_4). Upon distillation the ether, the residue is dissolved in 5 ml of abs. ethanol and hydrochloric ether is added to it up to a slightly acidic pH. While kept standing it is crystallized, then filtered, and it is recrystallized from an acetone ethanol mixture (lamellated crystals). Yield: 3,2 g. M. p.: 199—200 °C.

1-piperidino-3-(p-methylphenyl-)2-methyl-propanol-3-HCl (XXXI).

10 g of 1-piperidino-3(p-methylphenyl-)-methyl-propanone-3-HCl (Mydeton) is hydrogenated in 40 ml of abs. ethanol, in the presence of 1,5 g of Pd/C, at room temperature and atmospheric pressure. About 8 hours are needed to take up the calculated amount of hydrogen. It is filtered, concentrated to half, and kept in refrigerator. It is filtered, and washed with abs. acetone. Yield: 5,2 g. M. p.: 130—131 °C.

1-piperidino-3-(-p-methylphenyl-)-2-methyl-propene-3-HCl (XXXII).

3 g of hydroxy compound XXX is dissolved in 10 ml of acetic acid and it is refluxed in the presence of 1 ml of 9,4 N $HClO_3$ for 50 minutes. After cooling, another ml of $HClO_3$ is added and it is diluted until turbidity begins. The perchlorate of the unsaturated compound is crystallized while standing. Yield: 2,5 g. M. p.: 162 °C. The perchlorate is solved in 5 ml of acetone and alkalized with 2 N NaOH, then diluted with 10 ml of water and extracted with ether. The ether solution is washed with water, dried anhydrous (Na_2SO_4) and evaporeted. The oily residue after distillation, is dissolved in 5 ml of absolute acetone and ether-hydrochloric acid is added until a slightly acidic pH. While standing, the hydrochloride of the propene derivative crystallizes. Yield: 1,2 g. M. p.: 200 °C.

1-piperidino-3-(2-tetrahydro-(5, 6, 7, 8)-naphthyl-)propanone-3-HCl (XXXIII).

50 g of 2-acetyl-tetrahydro-(5, 6, 7, 8)-naphthalene (27), 34,8 g piperidine HCl and 15 g of paraformaldehyde are suspended in 150 ml of abs. ethanol and refluxed for 6 hours. The warm solution is filtered and evaporated to half at reduced pressure. 200 ml of abs. acetone is added to the residue and it is kept in a refrigerator. The next day it is filtered, washed with acetone and dried. Yield: 75 g. M. p.: 172—174 °C. Recrystallized from acetone-ethanole mixture, M. p.: 178,5 °C.

1-piperidino-3-(-2-tetrahydro-(5, 6, 7, 8) naphthyl-)propanol-3-HCl (XXXIV).

45 g of hydrochloride of XXXIII is dissolved in a mixture of 250 ml of water and 50 ml of ethanol. It is acidified with a few drops of HCl and reduced in the presence of 11 g of a Pd/C catalyst at atmospheric pressure. The calculated amount of hydrogen is taken up in about 18 hours. It is filtered and the filtrate is evaporated to 1/4 the volume at reduced pressure. The residue is rendered alkaline with 5% NaOH,

it is extracted with 4 ×60 ml of ether. The combined ether extracts are washed with water and dried with anhydrous Na_2SO_4. After evaporation of the ether 26 g of viscous oil remains, which is converted into the hydrochloride (in acetone solution with hydrochloric ether). The filtered crystalline substance is recrystallized from acetone. Yield: 33 g. M. p.: 168 °C.

1-piperidino-3-(-2-teirahydro (5, 6, 7, 8) naphthyl-)propene-3-HCl (XXXV).

5 g of XXXIV is dissolved in 15 ml of acetic acid and refluxed in the presence of 0,6 ml of 9,4 $HClO_3$ for one hour. After cooling an other ml of $HClO_3$ is added to the solution and diluted with water until the appearance of turbidity. The perchlorate of the base crystallizes while standing. Yield: 3,4 g. M. p.: 165—166 °C. Dissolved in acetone, it is rendered alkaline with 5% KOH, and it is extracted with ether. The ether solution is washed with water and dried (anhydrous Na_2SO_4). The dense oily residue is distilled and dissolved in 5 ml of absolute ethanol, it is acidified with hydrochloric ethanol, and ether is added until turbidity begins. While left standing lamellated crystals are precipitated from the solution, it is filtered and washed with little absolute acetone. M. p.: 224—225 °C.

1-(-beta-hydroxyethyl-aminomethyl-)-3-phenyl-propene-3-HCl (XXXVI).

5 g of cinnamic alcohol is added dropwise to 5,3 g of methylamino-ethanol in 10 minutes under constant. It is heated on a water bath for 40 minutes after the addition and kept standing for two hours at room temperature, it is diluted with 30 ml of water, then extracted with ether. The ether extract is washed with water and dried (anhydrous Na_2SO_4).

Evaporating the solvent, the oily residue is fractionated. The b. p. of the main fraction is 140 °C/4 mm. Yield: 5.1 g.
The HCl was obtained with alcoholic hydrochloric acid at 15—20 °C. M. p. of HCl: 121 °C.

1-(-beta-chlorethylaminomethyl-)-3-phenyl-propene-3-HCl (XXXVII).

9 g of thionylchloride is added to 5 g of XXXVI—HCl under cooling. Thereafter, it is heated, and refluxed for 1/2 hour.

The residue of the thionyl chloride is distilled *in vacuo*. The remaining brown, crystalline substance is solved in 30 ml of absolute acetone. On cooling, slightly brown crystals are precipitated.

It is filtered and recrystallized, m. p.: 147 °C. Yield: 3,8 g. (Special caution is advised because the substance induces inflammation of the skin.)

1-(-beta-piperidino-ethylamino-ethyl-)-3-phenyl-propene-3-2.HCl (XXXVIII).

10 g of piperidine is slowly dropped to 5 g of XXXVII—HCl, then refluxed for 2 hours, and kept at room temperature for one day, it is diluted with water and extracted with ether. The collected etheric extract was washed with water to remove the residue of piperidine and piperidine-HCl. It is dried (anhydrous Na_2SO_4), the ether evaporated and the residue dissolved in 30 ml of an acetone:ethanol mixture (1:1), it is acidified with HCl in dry ethanol to a slightly aceadic pH.

It is crystallized while kept standing. Small lamellae of mother-of- pearl color are obtained (3 g). M. p. of HCl is 248—250 °C.

1-(-p-i-propyl-)-phenyl-3-piperidino-propane-HCl (XXXIX).

27,9 g XIX is dissolved in 200 ml of absolute methanol and acidified with a small amount of HCl in dry ethanol and hydrogenated in the presence of 3 gr of Pd/C at atmospheric pressure. The hydrogenation is stopped after taking up the calculated amount of hydrogen. Having filtered the catalyst and evaporated the solvent in vacuo, about 70 ml, 23,6 g of white substance was filtered. M. p.: 203—204 °C. Further crystallized substance can be obtained from the mother liquor.

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ИЗУЧЕНИЕ ДЕЙСТВИЯ МЕЖДУ ФИЗИОЛОГИЧЕСКИМИ И ХИМИЧЕСКИМИ СТРОЕНИЯМИ ВЕЩЕСТВ, ДЕЙСТВУЮЩИХ НА ЦЕНТРАЛЬНЫЙ НЕРВНЫЙ МОЗГ. V

Синтез некоторых новых производных 1-(р-алкиларий)-3-трет.-амино-1-пропена и пропана

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Продолжая наши раннше синтетические исследования в области депрессантов центральной нервной системы (ц. н. с.), были получены при помощи реакции Фриделя—Крефца некоторые п-алкилацетофеноны и переведены реакцией Манниха в И-ниперидиноалкил-п-алкилфенилкетоны. Они восстановлены до спиртов и дегидратированы хлорной кислатой до пропенов, а после повторного каталитического восстановления были получены производные пропанов.

Фармакологически установлено, что многие из синтезированных соединений являются активными депрессантами ц. н. с.

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ABOUT SOME REACTIONS OF 4'-NITRO-2'-HYDROXY-CHALCON

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4'-nitro-2'-hydroxy chalcon was transformed into 7-nitro flavonol and chalcondibromide, prepared from chalcon by addition of bromine and was converted into 7-nitro-flavone by alkaline and hydrochloric acid ring closure.

The transformation of chalcondibromides prepared from chalcons containing an orto-hydroxyl group by adding bromine to flavone is widely known, as well as the alkaline H_2O_2 oxidation of chalcones yielding the corresponding flavonol.

These reactions have been realised in the nitro-hydroxy-chalcon group with 5'-nitro-2'-hydroxy chalcon [1]. The present work reports the above mentioned reactions with 4'-ntro-2'-hydroxy chalcon.

As to the reactions it is worthy to mention that 4'-nitro-2'-hydroxy chalcon dibromide can be prepared not only by cooling, but also at reflux-temperature with almost the same yield as in the former case. It should also be mentioned that hydrogen cyanide cannot be added to nitrohydroxy-chalcon or other chalcons applied by us for other investigations [2]. The failure of this reaction in the case of chalcons containing a nitro group has already been established by other authors, too [3].

Futhermore, it should be emphasized that 7-nitro-flavone can be prepared from 4'-nitro-2'-hydroxy chalcon dibromide not only by means of an alkaline, but also by hydrochloric acid ring closure. Flavone has not yet been prepared in this way from nitrohydroxy-chalcon dibromides, only from other chalcondibromides [4].

7-nitro-flavone obtained by us by alkaline and hydrochloric acid ring closure has been prepared otherwise, too [5].

Experimental

Experiments with hydrogen-cyanide addition. 0,27 g (1 mmole) 5'-nitro-2'-hydroxy-chalcon (m. p. 179 °C) was dissolved in 10 ml dimethyl-formamide and 0,07 ml glacial acetic acid was added. The solution was heated to 50 °C and dropwise an aqueous solution of 0,13 g (2 mmole) of KCN was added under constant stirring. Thereafter, the solution stirred for about 2 hours at the same temperature. It was kept for two days at room temperature, then diluted with distilled water, the precipitate was filtered, washed and after drying it was recrystallized from 1:1 mixture of ethanol-ethylacetate. M. p. 179 °C, M. p. of mixture: 179 °C, thus we recovered unchanged ketone.

The experiment was carried out with the above quantities by means of acidic cooling and boiling as like with chloroform aceton and metanol solutions on applying acidification by sulphuric acid. The initial substance was recovered in all these cases.

4'-nitro-2'-hydroxy-chalcondibromide. 0,27 g (1 mmole) chalcon was dissolved in 30 ml chloroform and 0,1 ml (0,31 g) (2 mmole) bromine was added. The solution was kept in a refrigerator for four hours at +5 °C, thereafter it was dried in vacuo and recrystallized from glacial acetic acid. Yellow needles were obtained. Yield: 0,34 g, 79%, M. p. 188 °C. Analyse: Calculated Br 37,2; Found 36,9%.

7-nitro-flavone. 0,1 g 4'-nitro-2'-hydroxy-chalcon dibromide was suspended in 5 ml methanol and 1 ml NaOH of a 10% aquous solution was added to this suspension. A substance formed which was recrystallized after washing with methanol from acetone. M. p. 233 °C. Analysis: Calculated C 67,4%, H 3,4%; Found C 67,4% H 3,4%.

0,1 g dibromide was boiled for 48 hours in a mixture of 40 ml etanol and 16 ml cc HCl. After cooling the separated substance was recrystallized from acetone, and a substance mp 233 °C, was obtained. There was no mp depression with flavone prepared by alkaline ring closure.

7-nitro-flavonol. 0,3 g 4'-nitro-2'-hydroxy-chalcon was dissolved in a mixture of 20 ml ethanol and 20 ml NaOH of 5%, then 5 ml of 17% H_2O_2 was added to the solution. After standing for a night at room temperature it was poured into 25 ml ice water and acidified with 1:1 HCl. The separated precipitate was recrystallized from glacial acetic acid and substance which did not melt till 250 °C was recovered. Analysis: C 67,9%; H 3,2%. Thus the substance is not flavonol, but its structure has not been clarified as yet.

From the filtrate of glacial acetic acid ester crystallization a crystalline substance was obtained by evaporation. Mp. 251 °C. According to analysis it is flavonol. Calculated C 63,6; H 3,2; Found C 63,9, H 3,4.

О НЕКОТОРЫХ РЕАКЦИЯХ 4'-НИТРО-2'-ГИДРОКСИ ХАЛКОНА

Дь. Щипош и Й. Йекл

4'-нитро-2'-гидрокси халкон был превращен щелечным окисленнем H_2O_2 в 7-нитрофлавонол, а халкон-дибромид, изготовлен из халкона присоединением брома был превращен в 7-нитрофлавон замыканием кольца щелечью и хлористоводородной кислотой.

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Erratum

to the paper J. HEVESI "On the Relative Yield and the Degree of Polarization of Viscous Fluorescent Solutions Quenched by KJ" published in Acta Phys. et Chem. Szeged, **8**, 16—24 (1962).

Figure 4 of the paper should be replaced by the following

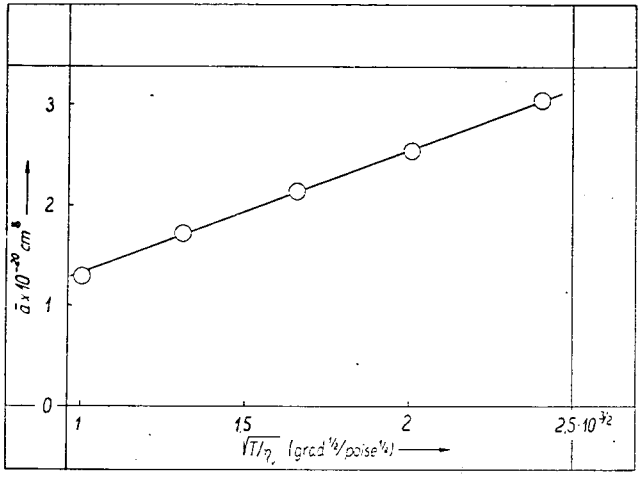

Fig. 4.

The experimental data used in the paper are quoted here (see J. Hevesi: Dissertation, Szeged, 1961. Table 9.):

t (°C)	$\bar{a}$ ($\times 10^{-20}$ cm^3)	$\sqrt{T/\eta_v} \cdot 10^{3/2}$ (grad$^{1/2}$/poise$^{1/2}$)
20	1,290	1,002
30	1,721	1,309
40	2,131	1,658
50	2,528	2,008
60	3,041	2,407

Kommunique

Viele unserer Leser haben sicherlich bereits Kenntnis genommen des Rundschreibens Nr. 2, in dem der IV. INTERNATIONALE KONGRESS FÜR GRENZFLÄCHENAKTIVE STOFFE angekündigt wurde, der in der Zeit vom 7. bis 12. September 1964 in Brüssel stattfindet.

Wie wir soeben erfahren, wird demnächst das Rundschreiben Nr. 3 erscheinen, in dem Einzelheiten über diesen Kongress bekanntgegeben werden.

Dieses Dokument enthält die Zusammensetzung der Komitees und insbesondere des Organisationskomitees, das von den Herren Dr. W. HAGGE (Deutschland), E. MAYOLLE (Frankreich) und Professor J. T. DAVIES (Großbritannien) geleitet wird.

Die Arbeiten des Kongresses sind in drei Sektionen aufgegliedert:

— *die Sektion A:* (in vier Gruppen unterteilt) unter Leitung von Herrn Professor Dr. Ing. F. ASINGER (Deutschland): *„Chemie der grenzflächenaktiven Stoffe"*; in dieser Sektion werden etwa fünfzig Vorträge gehalten werden.

— *die Sektion B:* (in sechs Gruppen unterteilt) unter Leitung von Herrn Professor Dr. J. Th. OVERBEEK (Niederlande): *„Physik der grenzflächenaktiven Stoffe"*; sie wird etwa einhundertfünfzig Vorträge umfassen.

— *die Sektion C:* (in sieben Gruppen unterteilt) unter Leitung von Herrn Professor C. PAQUOT (Frankreich): *„Anwendungstechnik der grenzflächenaktiven Stoffe"* mit etwa einhundert Vorträgen.

Diejenigen unserer Leser, die sich für diesen Kongress interessieren, können das Rundschreiben Nr. 3 sowie die Formulare für eine endgültige Anmeldung anfordern beim:

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